

EP1110988

**Title:**

**CATALYST FOR POLYESTER PRODUCTION AND PROCESS FOR  
PRODUCING POLYESTER WITH THE SAME**

**Abstract:**

A polyester having a good color tone, an excellent forming property and a high resistance to cohesion of foreign substance around a melt-spinning orifice when the polyester is melt-spun, is produced by polymerizing an aromatic difunctional carboxylic acid - alkylene glycol ester and/or oligomer thereof in the presence of a catalyst including a reaction product of (A) a Ti compound component including a Ti compound (1) of formula (I) or a Ti compound (2) produced by reacting the Ti compound (1) with an aromatic difunctional carboxylic acid of the formula (III) or anhydride thereof, with (B) a P compound component selected from P compound (3) of the formula (III). &lt;CHEM&gt; &lt;CHEM&gt; &lt;CHEM&gt; R<1> = C<sub>2</sub>-C<sub>10</sub>alkyl group; p = 1 - 3, n = 2 - 4, R<2> = substituted or unsubstituted C<sub>6</sub>-C<sub>20</sub>aryl or C<sub>1</sub>-C<sub>20</sub> alkyl group, m = 1 or 2, q = 0 or 1, and m + q = 1 or 2



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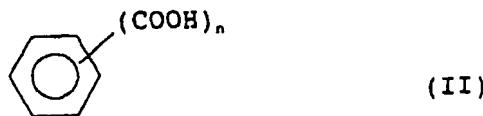
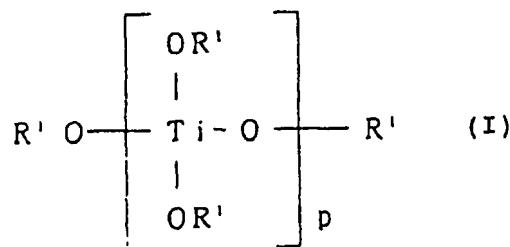
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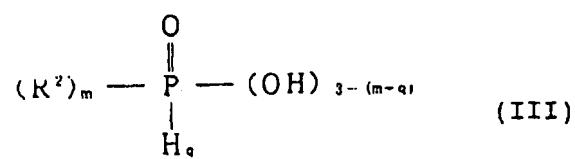
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London WC1A 2RA (GB)(54) **CATALYST FOR POLYESTER PRODUCTION AND PROCESS FOR PRODUCING POLYESTER  
WITH THE SAME**

(57) A polyester having a good color tone, an excellent forming property and a high resistance to cohesion of foreign substance around a melt-spinning orifice when the polyester is melt-spun, is produced by polymerizing an aromatic difunctional carboxylic acid - alkylene glycol ester and/or oligomer thereof in the presence of a catalyst including a reaction product of (A) a Ti compound component including a Ti compound (1) of formula (I) or a Ti compound (2) produced by reacting the Ti compound (1) with an aromatic difunctional carboxylic acid of the formula (III) or anhydride thereof, with (B) a P compound component selected from P compound (3) of the formula (III).



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[ $R^1 = C_2-C_{10}$  alkyl group;  $p = 1-3$ ,  $n = 2-4$ ,

$R^2 = \text{substituted or unsubstituted } C_6-C_{20} \text{ aryl or } C_1-C_{20} \text{ alkyl group, } m = 1 \text{ or } 2, q = 0 \text{ or } 1, \text{ and } m + q = 1 \text{ or } 2$ ]

**Description****TECHNICAL FIELD**

5 [0001] The present invention relates to a catalyst for producing a polyester and a process for producing the polyester by using the same. More particularly, the present invention relates to a catalyst for producing a polyester, comprising a specific titanium compound and a phosphorus compound, and a process for producing the polyester having a good color tone (b value), and thus not needing an addition of a cobalt compound to regulate the color tone, by using the catalyst.

**BACKGROUND ART**

10 [0002] The polyesters, particularly, polyethylene terephthalate, polyethylene naphthalate, polytrimethylene terephthalate and polytetramethylene terephthalate, have excellent mechanical, physical and chemical performances and thus are widely utilized for various fibers, films and other shaped articles.

15 [0003] For example, polyethylene terephthalate is usually produced by preparing an ethyleneglycol ester of terephthalic acid and/or oligomers of the ester by a direct esterification reaction of terephthalic acid with ethyleneglycol, or an interesterification reaction of a lower dialkyl ester of terephthalic acid, for example, dimethyl terephthalate, with ethyleneglycol, or a reaction of terephthalic acid with ethyleneoxide, and then by polymerizing ethyleneglycol ester of terephthalic acid and/or oligomer of the ester in the presence of a polymerization catalyst under a reduced pressure 20 at an elevated temperature, until the polymerization product obtains a target degree of polymerization. Also, the polyethylene naphthalate, polytrimethylene terephthalate and polytetramethylene terephthalate can be produced by a process similar to that mentioned above.

25 [0004] It is well known that the reaction rate of the polymerization reaction and the quality of the resultant polyester are greatly influenced by the type of the catalyst for the polymerization reaction step. As a polymerization catalyst for the polyethylene terephthalate, antimony compounds are most widely employed, because they exhibit excellent catalytic property for polymerization, and the resultant polyester has a good color tone.

30 [0005] However, when the antimony compounds are employed as a polymerization catalyst, the resultant polyester is disadvantageous in that when a melt-spinning procedure of the resultant polyester is continuously carried out for a long period, a foreign substance is cohered and accumulated around the melt-spinning orifice (which foreign substance will be referred to as an orifice foreign substance hereinafter), and causes the stream of the polymer melt extruded through the orifice to be bent (which will be referred to as a bending phenomenon of polymer melt stream hereinafter), and the bending phenomenon causes formation of fluffs and breakage of melt spun filaments to occur during the melt-spinning and drawing procedures. Namely, the shaping property of the polyester is degraded by the antimony compound 35 catalyst.

35 [0006] As a polymerization catalyst other than the antimony compounds, the utilization of titanium compounds, for example, titanium tetrabutoxide is suggested. When the titanium compound as mentioned above is employed, the problem of accumulation of the orifice foreign substance can be solved. However, this catalyst causes a new disadvantage in that the resultant polyester per se is colored yellowish and exhibits a poor stability to heat-melting.

40 [0007] To solve the above-mentioned coloring problem, generally, a cobalt compound is mixed into the polyester to erase the yellowish color. It is true that the color tone (apparent whiteness) of the polyester can be improved by mixing the cobalt compound into the polyester. However, the mixed cobalt compound causes the stability of the polyester to heat melting to be decreased and thus the resultant polyester to be easily decomposed.

45 [0008] As a titanium compound for catalyst for the production of the polyester, it is known to employ titanium hydroxide in Japanese Examined Patent Publication No. 48-2,229,  $\alpha$ -titanic acid in Japanese Examined Patent Publication No. 47-26,597.

50 [0009] However, in the former catalyst the titanium hydroxide is difficult to pulverize and in the latter catalyst,  $\alpha$ -titanic acid is easily modified and is difficult to store and handle. Thus, both the catalysts are not suitable for practical industrial use, and also the catalysts are seldom produce a polyester having a good color tone (b value).

55 [0010] Also, Japanese Examined Patent Publication No. 59-46,258 discloses that a product obtained by a reaction of a titanium compound with trimellitic acid is used as a catalyst for producing the polyester, and Japanese Unexamined Patent Publication No. 58-38,722 discloses that a product of titanium compound with a phosphite ester is usable as a catalyst for producing the polyester. It is true that both the processes enable the stability of the polyester for melting heat to be enhanced to some extent. However, the color tone (colorlessness) of the resultant polyester is unsatisfactory.

55 Thus, the color tone (b value) of the polyester must be further improved.

55 [0011] Further, Japanese Unexamined Patent Publication No. 7-138,354 discloses employment of a complex of a titanium compound with a phosphorus compound as a catalyst for producing the polyester. This process enables the stability of the resultant polyester to melting heat to some extent. However, the color tone of the resultant polyester is

unsatisfactory.

[0012] Furthermore, when the phosphorus-containing catalyst as mentioned above is employed, the catalyst per se is usually retained, as a foreign substance, in the resultant polyester polymer. Thus, this problem must be solved.

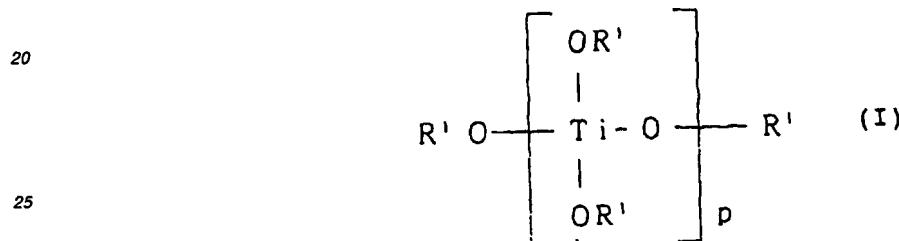
5 DISCLOSURE OF THE INVENTION

[0013] An object of the present invention to provide a catalyst for producing a polyester having a good color tone (b value), a low content of a foreign substance and an excellent melting heat stability, and a process for producing a polyester by using the same.

10 [0014] The above-mentioned object can be attained by the catalyst of the present invention for producing a polyester and the process of the present invention for producing a polyester by using the catalyst. The catalyst of the present invention for producing the polyester comprises a reaction product of

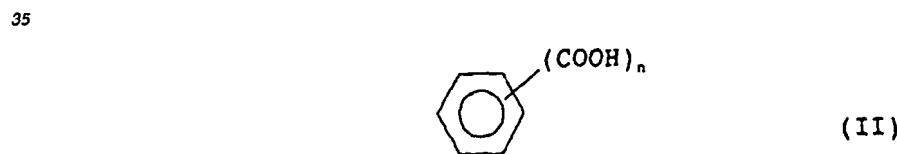
(A) a titanium compound component comprising at least one member selected from the group consisting of:

15 titanium compounds (1) represented by the general formula (I):



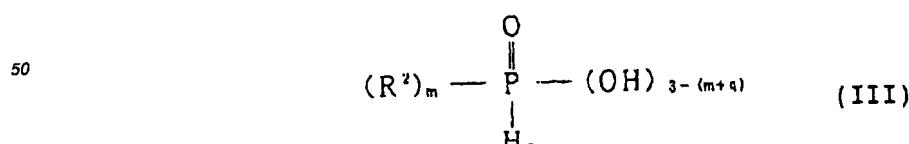
in which formula (I), R' represents an alkyl group having 1 to 10 carbon atoms and p represents an integer of 1 to 3, and

30 titanium compounds (2) produced by reacting the titanium compounds (1) of the formula (I) with aromatic polycarboxylic acids represented by the general formula (II):



in which formula (II), n represents an integer of 2 to 4, or anhydrides of the aromatic polycarboxylic acids of the formula (II), with

45 (B) a phosphorus compound component comprising at least one member selected from the phosphorus compounds (3) of the general formula (III):



55 in which formula (III), m represents an integer of 1 or 2, q represents an integer of 0 or 1, the sum of m and q, (m + q), is 1 or 2, R<sup>2</sup> represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms or alkyl group having 1 to 20 carbon atoms and when m represents 2, the two R<sup>2</sup> groups are the same as each other or different from each other.

[0015] The process of the present invention for producing a polyester comprises polymerizing a polymerization-starting material comprising at least one member selected from the group consisting of alkylene glycol esters of aromatic difunctional carboxylic acids and oligomers thereof in the presence of a catalyst, wherein the catalyst comprises a reaction product of

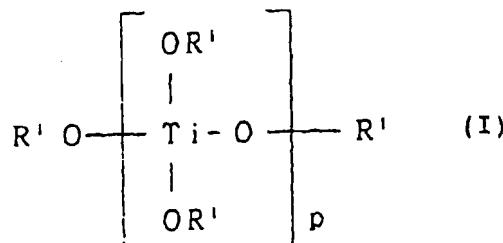
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(A) a titanium compound component comprising at least one member selected from the group consisting of:

titanium compounds (1) represented by the general formula (I):

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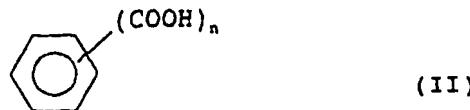
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in which formula (I), R' represents an alkyl group having 1 to 10 carbon atoms and p represents an integer of 1 to 3, and

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titanium compounds (2) produced by reacting the titanium compounds (1) of the formula (I) with aromatic polycarboxylic acids represented by the general formula (II):

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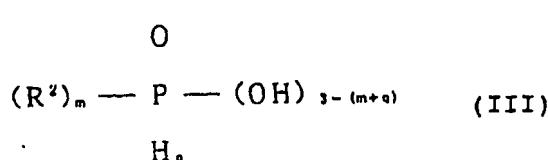


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in which formula (II), n represents an integer of 2 to 4, or anhydrides of the aromatic polycarboxylic acids of the formula (II), with

(B) a phosphorus compound component comprising at least one member selected from the phosphorus compounds (3) of the general formula (III):

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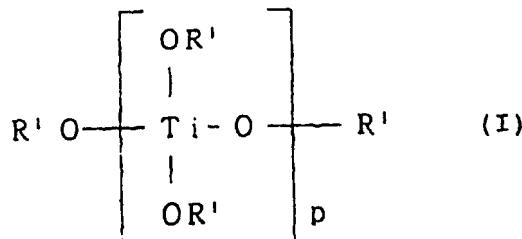
in which formula (III), m represents an integer of 1 or 2, q represents an integer of 0 or 1, the sum of m and q, (m + q), is 1 or 2, R<sup>2</sup> represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms or alkyl group having 1 to 20 carbon atoms and when m represent 2, the two R<sup>2</sup> groups are the same as each other or different from each other; and

the amount of the catalyst in terms of molar amount in millimole of titanium atoms contained in the catalyst corresponds to 10 to 40% of the amount in millimole of the aromatic difunctional carboxylic acids contained in the polymerization-starting material.

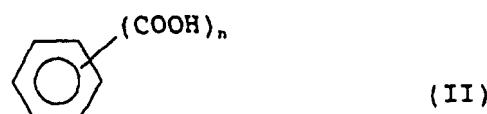
## 55 BEST MODE OF CARRYING OUT THE INVENTION

[0016] The catalyst of the present invention for producing a polyester comprises a reaction product of a titanium compound component (A) with a phosphorus compound component (B) which will be explained in detail hereinafter.

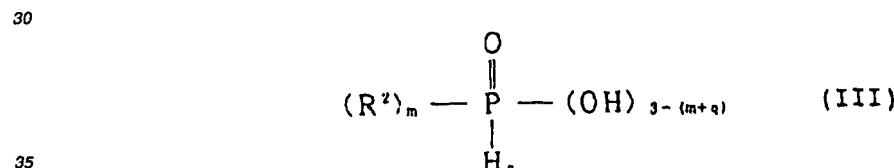
[0017] The titanium compound component (A) usable for the catalyst of the present invention comprises at least one member selected from the group consisting of titanium compounds (1) represented by the following general formula (I):



15 in which formula (I), R<sup>1</sup> represents an alkyl group having 2 to 10 carbon atoms, preferably 3 to 6 carbon atoms, p represents an integer of 1 to 3, preferably 1 to 2; and titanium compounds (2) obtained by reacting the titanium compounds (1) of the general formula (I) with aromatic polycarboxylic acids represented by the following general formula (II):



25 in which formula (II), n represents an integer of 2 to 4, preferably 2 to 3, or anhydrides of the aromatic polycarboxylic acid.  
 [0018] The phosphorus compound component (B) usable for the catalyst of the present invention comprises at least one member selected from the phosphorus compounds (3) represented by the following general formula (III):



40 in which formula (III), m represents an integer of 1 or 2, q represents an integer of 0 or 1, the sum of m and q is 1 or 2, R<sup>2</sup> represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms, preferably 6 to 10 carbon atoms, or alkyl group having 1 to 20 carbon atoms, preferably 2 to 12 carbon atoms, and when m represents an integer of 2, the two R<sup>2</sup> groups may be the same as each other or different from each other.

45 [0019] In the reaction product of the titanium compound component (A) with the phosphorus compound component (B), usable as a catalyst of the present invention for producing the polyester, preferably, in the reaction product of the titanium compound component (A) with the phosphorus compound component (B), the ratio m<sub>Ti</sub>/m<sub>P</sub> of the amount of the titanium compound component (A) in terms of a molar amount m<sub>Ti</sub> of titanium atoms to the amount of the phosphorus compound component (B) in terms of a molar amount m<sub>P</sub> of phosphorus atoms is in the range of from 1:1 to 1:4, more preferably 1:1.5 to 1:2.5.

50 [0020] The phrase "an amount (m<sub>Ti</sub>) of the titanium compound component (A) in terms of a molar amount of titanium atoms" refers to as a total sum of products of molar amounts of individual titanium compounds and the numbers of the titanium atoms per molecule contained in individual titanium compounds.

55 [0021] Also, the phrase "an amount (m<sub>P</sub>) of the phosphorus compound component (B) in terms of a molar amount of phosphorus atoms" refers to a total sum of products of molar amounts of individual phosphorus compounds and the numbers of the phosphorus atoms per molecule contained in the individual phosphorus compounds. The phosphorus compounds of the formula (III) contain only one phosphorus atoms per molecule of the individual phosphorus compounds. Thus, in this case, the amount of each phosphorus compound in terms of a molar amount of phosphorus atoms is the same as the real molar amount of each phosphorus compound.

[0022] When the reaction molar ratio m<sub>Ti</sub>/m<sub>P</sub> is more than 1:1, namely when the amount of the titanium compound component (A) is too much, the resultant catalyst may cause the polyester produced by using the catalyst to exhibit

an unsatisfactory color tone (apparent whiteness) and an insufficient heat resistance. Also, when the reaction molar ratio  $m_T/m_P$  is less than 1:4, namely when the amount of the titanium compound component (A) is too small, the resultant catalyst may exhibit an insufficient catalytic activity for the production of the polyester.

[0023] The titanium compounds (1) of the general formula (I) usable for the titanium compound component (A) include, titanium tetraalkoxides, for example, titanium tetrabutoxide, titanium tetraisopropoxide, titanium tetrapropoxide, and titanium tetraethoxide; and alkyl titanates, for example, octaalkyl trititanates and hexaalkyl dititanates. Among them, the titanium tetraalkoxides which have a high reactivity to the phosphorus compounds usable for the present invention are preferably employed. Particularly, titanium tetrabutoxide is more preferably employed for the present invention.

[0024] The titanium compounds (2) usable for the titanium compound component (A) is produced by reacting the titanium compounds (1) of the general formula (I) with aromatic polycarboxylic acids of the general formula (III) or anhydrides thereof. The aromatic polycarboxylic acids of the general formula (II) and the anhydrides thereof are preferably selected from phthalic acid, trimellitic acid, hemimellitic acid and pyromellitic acid and anhydrides of the above-mentioned acids. Particularly, trimellitic anhydride, which has a high reactivity to the titanium compounds (1) and enables the resultant polymerization product to exhibit a high affinity with the resultant polyester, is preferably employed.

[0025] The reaction of the titanium compounds (1) with the aromatic polycarboxylic acids or the anhydrides thereof can be carried out by mixing the aromatic polycarboxylic acids or anhydrides thereof into a solvent to cause a portion or all of the polycarboxylic acids or the anhydrides thereof to be solved in the solvent; adding dropwise the titanium compound (1) into the mixture; and heating the reaction mixture at a temperature of 0 to 200°C for 30 minutes or more, preferably at 30 to 150°C for 40 to 90 minutes.

[0026] In the reaction, there is no specific restriction to the reaction pressure, and the reaction can be sufficiently effected under the ambient atmospheric pressure. The solvent for the above-mentioned reaction may be selected from those capable of dissolving therein a portion or all amount of the compounds of the formula (II) or the anhydrides thereof. The solvent is preferably selected from ethyl alcohol, ethyleneglycol, trimethyleneglycol, tetramethyleneglycol, benzene and xylene.

[0027] There is no specific limitation to the reaction molar ratio of the titanium compounds (1) with the compounds of the formula (II) or anhydrides thereof. However, if the proportion of the titanium compound (1) is too high, the resultant polyester may exhibit an unsatisfactory color tone and too low a softening temperature. If the proportion of the titanium compound (1) is too low, the resultant catalyst may exhibit an insufficient catalytic activity for promoting the polymerization reaction.

[0028] Accordingly, the reaction molar ratio of the titanium compounds (1) to the compounds of the formula (II) or the anhydrides thereof is preferably 2/1 to 2/5. The reaction product of the above-mentioned reaction may be subjected to the reaction procedure with the above-mentioned phosphorus compound (3) without refining or after refining the reaction product by a recrystallization thereof with a recrystallizing agent, for example, acetone, methyl alcohol and/or ethyl acetate.

[0029] In the phosphorus compound (3) represented by the general formula (III) usable for the phosphorus compound component (B), the  $C_6$ - $C_{20}$  aryl groups or  $C_1$ - $C_{20}$  alkyl groups represented by  $R^2$  may have no substituent or one or more substituents. The substituents include, for example, a carboxyl group, alkyl groups, a hydroxyl group and an amino group.

[0030] The phosphorus compounds (3) of the general formula (III) are selected from the groups consisting of, for example, phenylphosphonic acid, methylphosphonic acid, ethylphosphonic acid, propylphosphonic acid, isopropylphosphonic acid, butylphosphonic acid, tolylphosphonic acid, xylolphosphonic acid, biphenylphosphonic acid, naphthylphosphonic acid, anthorylphosphonic acid, 2-carboxyphenylphosphonic acid, 3-carboxyphenylphosphonic acid, 4-carboxyphenylphosphonic acid, 2,3-dicarboxyphenylphosphonic acid, 2,4-dicarboxyphenylphosphonic acid, 2,5-dicarboxyphenylphosphonic acid, 2,6-dicarboxyphenylphosphonic acid, 3,4-dicarboxyphenylphosphonic acid, 3,5-dicarboxyphenylphosphonic acid, 2,3,4-tricarboxyphenylphosphonic acid, 2,3,5-tricarboxyphenylphosphonic acid, 2,3,6-tricarboxyphenylphosphonic acid, 2,4,5-tricarboxyphenylphosphonic acid, 2,4,6-tricarboxyphenylphosphonic acid, phenylphosphinic acid, methylphosphinic acid, ethylphosphinic acid, propylphosphinic acid, isopropylphosphinic acid, butylphosphinic acid, tolylphosphinic acid, xylolphosphinic acid, biphenylphosphinic acid, diphenylphosphinic acid, dimethylphosphinic acid, diethylphosphinic acid, dipropylphosphinic acid, diisopropylphosphinic acid, dibutylphosphinic acid, ditolylphosphinic acid, dixylolphosphinic acid, dibiphenylphosphinic acid, naphthylphosphinic acid, anthrilphosphinic acid, 2-carboxyphenylphosphinic acid, 3-carboxyphenylphosphinic acid, 4-carboxyphenylphosphinic acid, 2,3-dicarboxyphenylphosphinic acid, 2,4-dicarboxyphenylphosphinic acid, 2,5-dicarboxyphenylphosphinic acid, 2,6-dicarboxyphenylphosphinic acid, 3,4-dicarboxyphenylphosphinic acid, 3,5-dicarboxyphenylphosphinic acid, 2,3,4-tricarboxyphenylphosphinic acid, 2,3,5-tricarboxyphenylphosphinic acid, 2,3,6-tricarboxyphenylphosphinic acid, 2,4,5-tricarboxyphenylphosphinic acid, 2,4,6-tricarboxyphenylphosphinic acid, bis(2-carboxyphenyl)phosphinic acid, bis(3-carboxyphenyl)phosphinic acid, bis(4-carboxyphenyl)phosphinic acid, bis(2,3-dicarboxyphenyl)phosphinic acid, bis(2,4-dicarboxyphenyl)phosphinic acid, bis(2,5-dicarboxyphenyl)phosphinic acid, bis(2,6-dicarboxyphenyl)phosphinic acid, bis(3,4-dicarboxyphenyl)phosphinic acid, bis(3,5-dicarboxyphenyl)phosphinic acid, bis(2,3,4-tricarboxyphenyl)phosphinic acid.

phenyl)phosphinic acid, bis(2,3,5-tricarboxyphenyl)phosphinic acid, bis(2,3,6-tricarboxyphenyl)phosphinic acid, bis(2,4,5-tricarboxyphenyl)phosphinic acid, and bis(2,4,6-tricarboxyphenyl)phosphinic acid.

[0031] The preparation of the catalyst from the titanium compound component (A) and the phosphorus compound component (B) is carried out, for example, by mixing the component (B) comprising at least one phosphorus compound component (3) of the formula (III) into a solvent to dissolve a portion or all amount of the phosphorus compound component (B) in the solvent; adding dropwise the titanium compound component (A) into the component (B) mixture; and heating the resultant reaction system at a temperature of 0 to 200°C for a reaction time of 30 minutes or more, preferably 60 to 150°C for a reaction time of 40 to 90 minutes. In this reaction, there is no specific limitation to the reaction pressure. The reaction may be carried out under pressure (0.1 to 0.5 MPa), or the ambient atmospheric pressure, or a reduced pressure (0.001 to 0.1 Pa), but is usually carried out under the ambient atmospheric pressure.

[0032] The solvent usable for the component (A) comprising the phosphorus compound (3) of the formula (III) for the catalyst preparation is not limited to specific solvents as long as the solvent can dissolve therein at least a portion of the phosphorus compound component (B). Preferably, the solvent comprises at least one member selected from, for example, ethyl alcohol, ethyleneglycol, trimethyleneglycol, tetramethyleneglycol, benzene and xylene. Particularly, the solvent comprises a glycol compound the same as the glycol component from which the target polyester is prepared.

[0033] In the catalyst-preparation reaction as mentioned above, the mixing ratio of the titanium compound component (A) and the phosphorus compound component (B) in the reaction system is established so that in the reaction product produced from the titanium compound component (A) and the phosphorus compound component (B) and contained in the resultant catalyst, the ratio  $m_T/m_p$  of the amount of the titanium compound component (A) in terms of a molar amount  $m_T$  of titanium atoms contained in the component (A) to the amount of the phosphorus compound component (B) in terms of a molar amount  $m_p$  of the phosphorus atoms contained in the component (B) is in the range of from 1:1 to 1:4. A preferable reaction molar ratio  $m_T/m_p$  is in the range of 1:1 to 1:3.

[0034] The reaction product of the titanium compound component (A) with the phosphorus compound component (B) is isolated from the reaction system thereof by way of, for example, a centrifugal sedimentation treatment or, filtration and the isolated reaction product may be employed, without refining it, as a catalyst for the production of the polyester, or the isolated reaction product may be refined by, for example, recrystallizing the reaction product from a recrystallizing agent, for example, acetone, methyl alcohol and/or water, and the refined product may be employed as a catalyst.

[0035] In the process for producing the polyester of present invention, a polymerization-starting material comprising at least one member selected from alkylene glycol esters of aromatic difunctional carboxylic acids and polymers having a low degree of polymerization (oligomers) thereof, is polymerized in the presence of the above-mentioned catalyst.

[0036] In the process of the present invention for producing the polyester, the amount of the catalyst in terms of molar amount in millimoles of titanium atoms contained therein is established at 10 to 40% based on the total molar amount in millimoles of the aromatic difunctional carboxylic acids contained in the polymerization-starting material. The catalyst amount is preferably 10 to 25% on the same basis as mentioned above. If the catalyst is employed in an amount of less than 10%, the effect of the catalyst for promoting the polymerization reaction of the polymerization-starting material is insufficient, thus the production efficiency for the polyester is insufficient and thus a polyester having a target degree of polymerization is not obtained. Also, if the catalyst is employed in an amount of more than 40%, the resultant polyester has an unsatisfactory color tone, (b value) and is slightly colored yellowish and thus exhibits an unsatisfactory utilizability in practice.

[0037] In the alkylene glycol esters of the aromatic difunctional carboxylic acids usable as a polymerization-starting material for the process of the present invention for producing the polyester, the aromatic difunctional carboxylic acids are preferably selected from terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, biphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyletherdicarboxylic acid, diphenoxethanedicarboxylic acid, and  $\beta$ -hydroethoxybenzoic acid, more preferably terephthalic acid and naphthalenedicarboxylic acid. Also, the alkylene glycols are preferably selected from ethyleneglycol, trimethyleneglycol, tetramethyleneglycol, neopentylglycol and hexamethyleneglycol.

[0038] The alkylene glycol esters of the aromatic difunctional carboxylic acids and/or oligomers may be produced by any process. Usually, they are produced by heat-reacting an aromatic difunctional carboxylic acid or an ester-producing derivative thereof with an alkylene glycol or an ester-producing derivative thereof.

[0039] For example, ethyleneglycol ester of terephthalic acid and oligomers thereof which are used as a starting material for polyethylene terephthalate will be explained below. They are usually produced by directly esterifying terephthalic acid with ethyleneglycol, or by interesterifying a lower alkyl ester of terephthalic acid with ethyleneglycol or by addition-reacting terephthalic acid with ethylene oxide.

[0040] Also, trimethyleneglycol ester of terephthalic acid and/or oligomers thereof which are used as a starting material for polytrimethylene terephthalate will be explained below. They are usually produced by directly esterifying terephthalic acid with trimethyleneglycol, or by interesterifying a lower alkylester of terephthalic acid with trimethyleneglycol, or by addition reacting terephthalic acid with trimethyleneoxide.

[0041] The above-mentioned alkylene glycol esters of aromatic difunctional carboxylic acids and/or oligomers thereof,

may be employed together with other difunctional carboxylic esters copolymerizable with the above-mentioned esters or oligomers, as an additional component, in an amount of 10 molar% or less, preferably 5 molar% or less, based on the total molar amount of the acid component, as long as the additional component does not cause the effect of the process of the present invention to be substantially degraded.

5 [0042] The preferably copolymerizable additional component may be selected from esters of an acid component comprising at least one member selected from, for example, aliphatic and cycloaliphatic difunctional dicarboxylic acids, for example, adipic acid, sebatic acid and 1,4-cyclohexanedicarboxylic acid, and hydroxycarboxylic acids, for example,  $\beta$ -hydroxyethoxybenzoic acid and p-hydroxybenzoic acid with a glycol component comprising at least one member selected from aliphatic cycloaliphatic and aromatic diol compounds, for example, alkyleneglycols having 2 or more 10 carbon atoms, 1,4-cyclohexanedimethanol, neopentylglycol, bisphenol A and bisphenol S, and polyoxyalkyleneglycols, or anhydrides of the esters. The additional components may be employed alone or in a mixture of two or more thereof. The content of the additional components in the copolymers must be in the above-mentioned range.

15 [0043] In the process of the present invention for producing the polyester, a procedure in which the catalyst is added into the polymerization-starting material may be effected in any stage before the start of the polymerization reaction of an aromatic difunctional carboxylic acid-alkyleneglycol ester or an oligomer thereof, and the catalyst-adding procedure may be carried out by any conventional method. For example, after a preparation of an aromatic difunctional 20 carboxylic ester is completed, a solution or slurry of a catalyst may be added into the preparation system, to start a polymerization reaction, or the catalyst may be added into the reaction system, before the preparation of the aromatic difunctional carboxylic ester, together with the starting material or after the starting material is fed into the reaction system.

25 [0044] In the process of the present invention, there is no specific limitation to the conditions for the production of the polyester. Preferably, the polymerization reaction is carried out at a temperature of 230 to 320°C or under the ambient atmospheric pressure or a reduced pressure, for example, 0.1 Pa to 0.1 Mpa, or under the combined conditions of the above-mentioned temperature with the above-mentioned pressure, for 15 to 300 minutes.

30 [0045] In the process of the present invention, the reaction system is optionally added with a stabilizing agent, for example, trimethyl phosphate and further with another additive, for example, antioxidant, ultra-violet ray-absorbing agent, flame-retardant, fluorescent brightening agent, delustering agent, color tone-regulating agent and anti-foaming agent at any stage in the polyester production procedure.

35 [0046] Further, to finely regulate the color of the polyester, during the polyester production procedure, a color tone-regulating agent comprising at least one member selected from organic blue-coloring pigments, for example, ago, triphenylenethane, quinoline, anthraquinone and phthalocyanine blue-coloring pigments, and inorganic blue-coloring pigments may be mixed into the reaction system. Also, in the process of the present invention for producing the polyester, a conventional cobalt-containing inorganic blue-coloring pigment, which causes the melting heat stability of polyester to be decreased, is not necessary as a color tone regulating agent to the polyester, and thus the resultant polyester of the present invention is preferably substantially free from cobalt.

40 [0047] The polyester obtained by the process of the present invention usually exhibits an L value of 80.0 or more and a b value of -2.0 to 5.0, determined by a HUNTER color difference meter. If the L value is less than 80.0, the resultant polyester may exhibit too low a whiteness and thus may not form a shaped polyester article having a high whiteness and useful in practical use. Also, if the b value is less than -2.0, the resultant polyester may have too high a blueing effect whereas the yellowing effect of the polyester may be low. Further, if the b value is more than 5.0, the resultant polyester may exhibit too high a yellowing effect and thus may not be subjected to the production of a practically useful shaped polyester article.

45 [0048] In the polyester produced by the process of the present invention, the L value is preferably 82 or more, more preferably 83 or more, and the b value is preferably -1.0 to 4.5, more preferably 0.0 to 4.0.

[0049] The L value and b value of the polyester obtained by the process of the present invention is determined by the following method.

50 [0050] Namely, a sample of the polyester is melted at a temperature of 290°C under vacuum for 10 minutes, the polyester melt is formed into a plate having a thickness of  $3.0 \pm 1.0$  mm on an aluminum plate and, immediately after the forming, the polyester plate is cooled in ice water, the cooled plate is dried at 160°C for one hour, the dried plate is subjected to a crystallization treatment, the resultant plate is placed on a plate having a standard whiteness and for providing a color difference meter ready for use and the color tone of the surface of the plate was measured by a HUNTER color difference meter (model: CR-200, made by MINOLTA CO.).

55 [0051] The polyester produced by the process of the present invention contains substantially no cobalt atoms derived from a color tone-regulating cobalt compound. The cobalt atom-containing polyester is disadvantageous in that polyester exhibits a low melting heat stability and is easily decomposed. The phrase "a polyester containing substantially no cobalt atoms" refers to a polyester produced without employing a cobalt compound as a color tone-regulating agent or a polymerization catalyst and thus containing no cobalt atoms derived from the above-mentioned cobalt compound. Therefore, the polyester of the present invention may contain cobalt atoms derived from a cobalt compound added to

the polyester for a purpose other than the purposes of the color tone-regulating agent and the catalyst.

[0052] The polyester of the present invention preferably has a content of solid foreign particles having an average particle size of 3  $\mu\text{m}$  or more limited to 500 particles/g or less. When the foreign particle content is limited to 500 particles/g or less, blockage of a filter for the melt-shaping procedure and an increase in back pressure in the melt-spinning procedure are significantly restricted. The content of the foreign particles is more preferably 450 particles/g or less, still more preferably 400 particles/g or less.

[0053] In the polyester of the present invention, when heated in a nitrogen gas atmosphere at a temperature of 290°C for 15 minutes, preferably the number of breakage of backbone chains of the polyester molecules is limited to 4.0 equivalents/1,000 kg or less. When the breakage number of the backbone chains of the polyester molecules is 4.0 equivalents/1,000 kg or less, the deterioration of the polyester during the melt-shaping procedures is significantly restricted and thus the mechanical properties and the color tone of the shaped article can be improved. The above-mentioned breakage number of the backbone chains of the polyester molecules is more preferably 3.8 equivalents/1,000 kg or less, still more preferably 3.5 equivalents/1,000 kg or less.

[0054] In the polyester of the present invention, there is no specific limitation to the intrinsic viscosity thereof. Usually, the intrinsic viscosity of the polyester is preferably in the range of from 0.55 to 1.0. When the intrinsic viscosity is in the above-mentioned range, the melt-processing can be easily carried out and the resultant shaped article exhibits a high mechanical strength. The above-mentioned intrinsic viscosity of the polyester is more preferably in the range of from 0.60 to 0.90, still more preferably from 0.62 to 0.80.

[0055] The intrinsic viscosity of the polyester is determined in a solution in orthochlorophenol at a temperature of 35°C.

## EXAMPLES

[0056] The present invention will be further illustrated by the following examples which are not intended to restrict the scope of the present invention. In the examples, the intrinsic viscosity, the color tone, the titanium content of catalyst, the number of foreign particles, a layer of foreign matter adhered around a melt-spinning orifice and the melting heat stability, as mentioned above were determined by the following measurements.

### (1) Intrinsic viscosity

[0057] The intrinsic viscosity of a polyester polymer was determined from viscosities of solutions of the polyester polymer in orthochlorophenol measured at a temperature of 35°C.

### (2) Color tone (L value and b value).

[0058] A sample of a polymer was melted at a temperature of 290°C under vacuum for 10 minutes, the melted polymer was formed into a plate having a thickness of  $3.0 \pm 1.0$  mm on an aluminum plate and, immediately after the forming, the polymer plate was rapidly cooled in ice water, the cooled plate was subjected to a crystallization treatment at 160°C for one hour, the crystallized polymer plate was placed on a plate having a standard whiteness and for making a color difference meter (HUNTER type color difference meter, model: CR-200, made by MINOLTA CO.) ready for use, and the Hunter L value and b value of the polymer plate surface was measured by using the color difference meter. The L value represents a brilliance, and the larger the L value, the higher the brilliance. The larger the b value, the higher the degree of yellowing effect.

### (3) Titanium content of catalyst

[0059] The titanium content of a catalyst compound was determined by using a fluorescent X-ray measurement apparatus (model: 3270 made by RIGAKU K.K.)

### (4) Melting heat stability

[0060] Polyester pellets were placed in a glass tube having an outside diameter of 10 mm, an inside diameter of 8 mm and a length of 250 mm and immersed in a bath, in a nitrogen gas atmosphere, at 290°C for 15 minutes to melt it. A difference in intrinsic viscosity of the polyester pellets between before and after the heat-treatment as mentioned above was determined. From the intrinsic viscosity differences the number (equivalent) of the breakages of the backbone chains of the polyester molecules per 1,000 kg of the polyester polymer was calculated in accordance with the following equation:

**Breakage number of  
backbone chains (eq./1,000 kg)**

$$5 \quad = \left\{ \left[ \frac{IV_1}{3.07 \times 10^{-4}} \right]^{-1.30} - \left[ \frac{IV_0}{3.07 \times 10^{-4}} \right]^{-1.30} \right\} \times 10^{-6}$$

10 in which equation,  $IV_0$  represents an intrinsic viscosity of the polyester before the heat treatment and  $IV_1$  represents an intrinsic viscosity of the polyester after the heat treatment.

(5) Layer of foreign matter adhered around a melt-extruding orifice.

15 [0061] A polyester was pelletized and melted at 290°C, and the polyester melt was extruded through 12 orifices each having a hole diameter of 0.15 mm, at a taking-up speed of 600 m/min, for 2 days.

[0062] The height of a layer of foreign matter adhered to the periphery of the melt-extruding orifice was measured.

20 [0063] The higher the adhered foreign matter layer, the lower the resistance of the extruded filamentary streams of the polyester melt to bending, and the lower the shaping property of the polyester. Namely, the height of the adhered foreign matter layer is a parameter of the shaping property of the polyester.

(6) The number of foreign particles

25 [0064] A sample of a polymer in an amount of 100 mg was dissolved in 20 ml of hexafluoroisopropanol and the resultant solution was filtered through a polytetrafluoroethylene membrane filter having an opening size of 3 µm and a diameter of 2.5 cm (trademark: T300A, made by ADVANTEC K.K.) at a temperature of 25°C under a reduced pressure of 2.6 kPa. The number of foreign particles collected on the filter was counted by using an optical microscope, and the content of the foreign particles per g of the polymer was calculated.

30 Example 1

Preparation of catalyst (A)

35 [0065] Ethyleneglycol in an amount of 2.5 parts by weight was dissolved in 0.8 part by weight, and then into the resultant solution, titanium tetrabutoxide in an amount of 0.7 part by weight (corresponding to 0.5 molar% based on the molar amount of trimellitic anhydride) was added dropwise. Then the resultant reaction system was maintained at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. Thereafter, the reaction system was cooled to room temperature, and was mixed with 15 parts by weight of acetone and the resultant precipitation was collected by filtration and dried at a temperature of 100°C for 2 hours. The 40 resultant reaction product (titanium compound (2)) had a titanium content of 11.5% by weight.

[0066] Then, 3.6 parts by weight of phenylphosphonic acid were dissolved in 131 parts by weight of ethyleneglycol by heating at a temperature of 120°C for 10 minutes. The resultant ethyleneglycol solution in an amount of 134.5 parts by weight was further added with 40 parts by weight of ethyleneglycol, and in the resultant solution, 5.0 parts by weight of the above-mentioned titanium compound (2) were dissolved. The resultant reaction system was agitated at a temperature of 120°C for 60 minutes to produce a reaction product of the titanium compound (2) with phenylphosphonic acid. A white-colored slurry of a catalyst (A) containing the reaction product was obtained. The slurry of the catalyst (A) had a titanium content of 0.3% by weight.

Preparation of a polyester

50 [0067] Terephthalic acid in an amount of 166 parts by weight and ethyleneglycol in an amount of 75 parts by weight were subjected to an esterification reaction with each other at a temperature of 240°C, the resultant reaction product was placed in a polymerization flask equipped with a refining distillation column, and was mixed with the slurry of catalyst (A) as a polymerization catalyst, in an amount of 0.95 parts by weight (corresponding to  $20 \times 10^{-3}$  molar% in terms of titanium atoms based on the molar amount of terephthalic acid) and with a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmosphere pressure for 30 minutes; further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes; and still further heated at the above-

mentioned temperature for 110 minutes while the reaction pressure was gradually reduced and the reaction system was agitated, to complete the reaction. When the reaction was completed, the inside temperature of the flask was 285°C and the final reaction pressure was 49.3 Pa (0.37 mmHg). The resultant polyester had an intrinsic viscosity of 0.640.

5 [0068] The test results are shown in Table 1.

Examples 2 to 5 and Comparative Examples 1 to 4

10 [0069] In each of Example 2 to 5 and Comparative Examples 1 to 4, a catalyst was prepared by the same procedures as in Example 1 and a polyester was prepared by the same procedures as in Example 1, except that the P/Ti molar ratio of the catalyst, and the amount of the catalyst used in the polyester production were changed to those as shown in Table 1. The test results are shown in Table 1.

Example 6

15 Preparation of catalyst (B)

20 [0070] A mixture of 153 parts by weight of ethyleneglycol with 3.2 parts by weight of phenylphosphonic acid was heated at 120°C for 10 minutes to provide a solution. Into 134.6 parts by weight of the ethyleneglycol solution, 3.4 parts by weight of titanium tetrabutoxide were added dropwise, and the resultant reaction system was agitated at a temperature of 120°C for 60 minutes. A white-colored slurry containing a titanium compound (1) was obtained as a catalyst (B). The slurry had a titanium content of 0.3% by weight.

Preparation of a polyester

25 [0071] A polyester was prepared by the same procedures as in Example 1, except that the catalyst (B) produced by the above-mentioned procedures was employed as the polymerization catalyst. The test results are shown in Table 1.

Example 7

30 Preparation of a polyester

35 [0072] A reaction vessel equipped with a refining distillation column was charged with 194 parts by weight of dimethyl terephthalate, 124 parts by weight of ethyleneglycol and 0.12 part by weight of calcium acetate; the charged mixture was subjected to an interesterification reaction at a temperature of 220°C; after the resultant methyl alcohol in a theoretical quantity was removed by evaporation, the reaction mixture was added with 0.09 part by weight of phosphoric acid, to complete a first stage of reaction. Then the above-mentioned reaction mixture was placed in a polymerization flask equipped with a refining distillation column, and mixed with a polymerization catalyst consisting of the catalyst (A) slurry prepared by the same procedures as in Example 1 in an amount of 3.2 parts by weight (corresponding to a content of titanium compound (2) in terms of molar amount of titanium atoms of  $20 \times 10^{-3}\%$ , based on the molar amount of dimethyl terephthalate) and a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmospheric pressure for 30 minutes and further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes to proceed the reaction; and after the inside pressure of the reaction system was gradually reduced, and the reaction system was still further heated at the above-mentioned temperature for 110 minutes while agitating the reaction system, to complete the reaction. In the flask, the final inside temperature was 285°C and the final inside pressure was 49.3 Pa (0.37 mmHg).

40 [0073] The resultant polyester had an intrinsic viscosity of 0.640. The test results of the polyester are shown in Table 1.

45 50 Comparative Example 5

55 [0074] A polyester was prepared by the same procedures as in Example 7, except that, as a polymerization catalyst, titanium tetrabutoxide was employed, and the catalyst content and the amount of the catalyst slurry was controlled so that the amount of this catalyst in terms of molar amount of titanium atoms became  $20 \times 10^{-3}\%$  based on the molar amount of dimethyl terephthalate. The test results are shown in Table 1.

Example 8Preparation of a polyester

5 [0075] A polyester was prepared by the same procedures as in Example 7 except that, as a polymerization catalyst, the same catalyst (B) slurry as in Example 6 was employed.

[0076] The test results are shown in Table 1.

Comparative Example 6Preparation of a catalyst (C)

10 [0077] Trimellitic anhydride was dissolved in an amount of 0.80 part by weight in ethyl alcohol. Into the resultant solution, 0.64 part by weight of titanium tetrabutoxide was added dropwise, and the resultant reaction system was held 15 in the air atmosphere under the ambient atmospheric pressure at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. After the reaction and the aging, the reaction system was cooled to room temperature and mixed with 15 parts by weight of acetone, and the resultant precipitation was collected by filtration. The resultant catalyst (C) had a titanium content of 12% by weight.

Preparation of a polyester

20 [0078] A polyester was prepared by the same procedures as in Example 7, except that, as a polymerization catalyst, the above-mentioned catalyst (C) was employed and the catalyst concentration and the amount of the catalyst (C) slurry were controlled so that the amount of the catalyst (C) in terms of molar amount of titanium atoms become  $20 \times 10^{-3}$  based on the molar amount of dimethyl terephthalate.

[0079] The test results are shown in Table 1.

Comparative Example 7Preparation of a catalyst (D)

25 [0080] A catalyst (D) was prepared by the same procedures as those for the catalyst (A) disclosed in Example 1, except that 3.6 parts by weight of phenylphosphonic acid were replaced by 3.6 parts by weight of phenyl phosphite. A white-colored slurry of the catalyst (D) was obtained. The slurry had a titanium content of 0.3% by weight.

Preparation of a polyester

35 [0081] A polyester was prepared by the same procedures as in Example 7, except that as a polymerization catalyst, the catalyst (D) produced by the above-mentioned procedures was employed in an amount of 3.2 parts by weight (corresponding to a molar amount of titanium atoms of  $20 \times 10^{-3}$  based on the molar amount of dimethyl terephthalate). The test results are shown in Table 1.

Comparative Example 8

40 [0082] A polyester was prepared by the same procedures as in Example 7, except that as a polymerization catalyst, diantimony trioxide was employed, and the content of the catalyst in the catalyst slurry and the amount of the catalyst slurry were established so that the molar amount of antimony atoms contained in the catalyst slurry was adjusted to  $27 \times 10^{-3}$  based on the molar amount of dimethyl terephthalate.

[0083] The test results are shown in Table 1.

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Table 1

Item	Catalyst		Properties of polyester				Height of foreign matter layer adhered around melt-spinning orifice ( $\mu\text{m}$ )		
	P/Ti molar ratio	Amount of catalyst ( $\text{x}^{-3}\%$ )	Intrinsic viscosity (dl/g)	Color tone L	Breakage number of backbone chains (eq./1,000 kg)	The number of foreign particles (particles/g)			
Example No.	1	2.0	20	0.640	86.0	1.7	3.0	320	5
	2	1.0	20	0.640	85.6	2.2	3.4	290	7
	3	3.0	20	0.641	86.0	2.5	2.7	340	6
	4	2.0	10	0.639	85.4	2.5	2.3	280	6
	5	2.0	30	0.639	85.2	3.2	3.6	360	7
	6	2.0	20	0.640	85.0	4.0	3.0	330	8
	7	2.0	20	0.640	85.2	4.2	3.8	380	9
	8	2.0	20	0.640	85.3	4.4	4.2	400	9
Comparative Example	1	0.5	20	0.640	85.4	7.4	5.7	420	9
	2	3.5	20	Reaction was not carried out.					
	3	2.0	5	Reaction was not carried out.					
	4	2.0	45	0.640	84.1	7.2	5.0	520	9
	5	-	20	0.640	82.1	9.3	5.9	720	5
	6	-	20	0.640	84.2	5.2	5.3	590	8
	7	2.0	20	0.640	84.1	5.8	3.6	530	9
	8	( $\text{Sb}_2\text{O}_3$ )	25	0.639	84.5	0.3	3.5	400	49

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Example 9Preparation of catalyst (E)

40 [0084] Ethyleneglycol in an amount of 2.5 parts by weight was dissolved in 0.8 part by weight of trimellitic anhydride; into the resultant solution, titanium tetrabutoxide in an amount of 0.7 part by weight (corresponding to 0.5 molar% based on the molar amount of trimellitic anhydride) was added dropwise, the resultant reaction system was maintained at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. Thereafter, the reaction system was cooled to room temperature, and was mixed with 15 parts by weight of acetone, the resultant precipitation was collected by filtration through a No. 5 filter paper and dried at a temperature of 100°C for 2 hours. The resultant reaction product (titanium compound (2)) had a titanium content of 11.5% by weight.

45 [0085] Then, 5.6 parts by weight of 3,5-dicarboxyphenylphosphonic acid were mixed into 129 parts by weight of ethyleneglycol and dissolved by heating at a temperature of 120°C for 10 minutes. The resultant ethyleneglycol solution in an amount of 134.5 parts by weight was further added with 40 parts by weight of ethyleneglycol, and in the resultant solution, 5.0 parts by weight of the above-mentioned titanium compound (2) were dissolved. The resultant reaction system was agitated at a temperature of 120°C for 60 minutes. A slightly yellowish transparent solution of a catalyst (E) was obtained. The catalyst (E) solution had a titanium content of 0.3% by weight.

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Preparation of a polyester

[0086] Terephthalic acid in an amount of 166 parts by weight and ethyleneglycol in an amount of 75 parts by weight were subjected to an esterification reaction with each other at a temperature of 240°C, the resultant reaction product was placed in a polymerization flask equipped with a refining distillation column, and was mixed with the solution of

5 catalyst (E) as a polymerization catalyst, in an amount of 0.95 parts by weight (corresponding to  $20 \times 10^{-3}$  molar% in terms of a molar amount of titanium atoms based on the molar amount of terephthalic acid) and with a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmospheric pressure for 30 minutes; further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes; and still further heated at the above-mentioned temperature for 110 minutes while the reaction pressure was gradually reduced and the reaction system was agitated, to complete the reaction. When the reaction was completed, the inside temperature of the flask was 285°C and the final reaction pressure was 49.3 Pa (0.37 mmHg). The resultant polyethylene terephthalate had an intrinsic viscosity of 0.640.

10 [0087] The test results are shown in Table 2.

Examples 10 to 13 and Comparative Examples 9 to 12

15 [0088] In each of Examples 10 to 13 and Comparative Examples 9 to 12, a catalyst (A) was prepared by the same procedures as for the catalyst (E) in Example 9 and a polyester was prepared by the same procedures as in Example 9, except that the P/Ti molar ratio of the catalyst, and the amount of the catalyst used in the polyester production were changed to those as shown in Table 2. The test results are shown in Table 2.

Example 14

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Preparation of catalyst (F)

25 [0089] A mixture of 151.2 parts by weight of ethyleneglycol with 5.0 parts by weight of 3,5-dicarboxyphenylphosphonic acid was heated at 120°C for 10 minutes to provide a solution. Into 134.6 parts by weight of ethyleneglycol solution 3.4 parts by weight of titanium tetrabutoxide were added dropwise, and the resultant reaction system was agitated at a temperature of 120°C for 60 minutes. A slight-yellowish transparent solution of a catalyst (F) was obtained. The catalyst (F) solution had a titanium content of 0.3% by weight.

Preparation of a polyester

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[0090] A polyester was prepared by the same procedures as in Example 9, except that the catalyst (F) produced by the above-mentioned procedures was employed as the polymerization catalyst. The test results are shown in Table 2.

Example 15

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Preparation of a polyester

40 [0091] A reaction vessel equipped with a refining distillation column was charged with 194 parts by weight of dimethyl terephthalate, 124 parts by weight of ethyleneglycol and 0.12 part by weight of calcium acetate; the charged mixture was subjected to an interesterification reaction at a temperature of 220°C; after the resultant methyl alcohol in a theoretical quantity was removed by evaporation, the reaction mixture was added with 0.09 part by weight of phosphoric acid, to complete a first stage of reaction. Then the above-mentioned reaction mixture was placed in a polymerization flask equipped with a refining distillation column, and mixed with a polymerization catalyst consisting of the catalyst (E) solution in an amount of 3.2 parts by weight (corresponding to a molar amount of titanium atoms of  $20 \times 10^{-3}$ % based on the molar amount of dimethyl terephthalate) and a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmospheric pressure for 30 minutes and further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes to proceed the reaction; and after the inside pressure of the reaction system was gradually reduced, and the reaction system was still further heated at the above-mentioned temperature for 110 minutes while agitating the reaction system, to complete the reaction. In the flask, the final inside temperature was 285°C and the final inside pressure was 49.3 Pa (0.37 mmHg).

45 [0092] The resultant polyethylene terephthalate had an intrinsic viscosity of 0.640. The test results of the polyester are shown in Table 2.

Example 16Preparation of a polyester

[0093] A polyester was prepared by the same procedures as in Example 15, except that as a polymerization catalyst, the catalyst (E) solution was replaced by the catalyst (F) solution.

[0094] The test results are shown in Table 2.

Table 2

Item	Catalyst		Properties of polyester					Height of foreign matter layer adhered around melt-spinning orifice (μm)	
	P/Ti molar ratio	Amount of catalyst (x <sup>-3</sup> %)	Intrinsic viscosity (dl/g)	Color tone L	Breakage number of backbone chains b	The number of foreign particles (eq./1,000 kg)	(particles/g)		
Example No.	9	2.0	20	0.640	86.0	1.5	2.9	300	5
	10	1.0	20	0.639	85.8	2.0	3.3	300	6
	11	3.0	20	0.639	86.2	2.2	2.6	330	8
	12	2.0	10	0.641	85.3	2.3	2.3	290	8
	13	2.0	30	0.640	85.2	3.0	3.6	360	9
	14	2.0	20	0.640	84.9	3.6	2.9	340	7
	15	2.0	20	0.640	85.2	4.0	3.6	390	9
	16	2.0	20	0.639	85.4	4.1	4.0	410	9
Comparative Example	9	0.5	20	0.640	85.2	7.7	5.6	420	10
	10	3.5	20	Reaction was not effected.					
	11	2.0	5	Reaction was not effected.					
	12	2.0	45	0.640	84.0	7.2	4.9	540	10

Example 17Preparation of catalyst (G)

[0095] Ethyleneglycol in an amount of 2.5 parts by weight was dissolved in 0.8 part by weight of trimellitic anhydride; into the resultant solution, titanium tetrabutoxide in an amount of 0.7 part by weight (corresponding to 0.5 molar% based on the molar amount of trimellitic anhydride) was added dropwise, the resultant reaction system was maintained at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. Thereafter, the reaction system was cooled to room temperature, and was mixed with 15 parts by weight of acetone, the resultant precipitation was collected by filtration through a No. 5 filter paper and dried at a temperature of 100°C for 2 hours. The resultant reaction product (titanium compound (2)) had a titanium content of 11.5% by weight.

[0096] Then, 5.2 parts by weight of diphenylphosphinic acid were dissolved in 136 parts by weight of ethyleneglycol by heating at a temperature of 120°C for 10 minutes. The resultant ethyleneglycol solution in an amount of 141.2 parts by weight was further added with 40 parts by weight of ethyleneglycol and, in the resultant solution, 5.0 parts by weight of the above-mentioned titanium compound (2) were dissolved. The resultant reaction system was agitated at a temperature of 120°C for 60 minutes to produce a reaction product of the titanium compound (2) with diphenylphosphinic acid. A slightly yellowish transparent solution of a catalyst (G) was obtained. The slurry of the catalyst (G) solution had a titanium content of 0.3% by weight.

Preparation of a polyester

[0097] Terephthalic acid in an amount of 166 parts by weight and ethyleneglycol in an amount of 75 parts by weight were subjected to an esterification reaction with each other at a temperature of 240°C, the resultant esterification

product was placed in a polymerization flask equipped with a refining distillation column, and was mixed with the catalyst (G) solution in an amount of 0.95 parts by weight (corresponding to  $20 \times 10^{-3}$  molar% of a molar amount of titanium atoms based on the molar amount of terephthalic acid) and with a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmospheric pressure for 30 minutes; further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes; and still further heated at the above-mentioned temperature for 110 minutes while the reaction pressure was gradually reduced and the reaction system was agitated, to complete the reaction. When the reaction was completed, the final inside temperature of the flask was 285°C and the final reaction pressure was 49.3 Pa (0.37 mmHg). The resultant polyethylene terephthalate had an intrinsic viscosity of 0.640.

10 [0098] The test results are shown in Table 3.

#### Examples 18 to 21 and Comparative Examples 13 to 16

15 [0099] In each of Example 18 to 21 and Comparative Examples 13 to 16, a catalyst was prepared by the same procedures as for the catalyst (G) in Example 17 and a polyester was prepared by the same procedures as in Example 17, except that the P/Ti molar ratio of the catalyst, and the amount of the catalyst used in the polyester production were changed to those as shown in Table 3. The test results are shown in Table 3.

#### Example 22

##### Preparation of catalyst (H)

20 [0100] A mixture of 147.3 parts by weight of ethyleneglycol with 4.4 parts by weight of diphenylphosphinic acid was heated at 120°C for 10 minutes to provide a solution. Into 151.7 parts by weight of the ethyleneglycol solution, 3.4 parts by weight of titanium tetrabutoxide were added dropwise, and the resultant reaction system was heated and agitated at a temperature of 120°C for 60 minutes. A slightly yellowish transparent solution containing a catalyst (H) was obtained. The catalyst (H) solution had a titanium content of 0.3% by weight.

##### Preparation of a polyester

30 [0101] A polyester was prepared by the same procedures as in Example 17, except that the catalyst (H) produced by the above-mentioned procedures was employed as the polymerization catalyst. The test results are shown in Table 3.

#### Example 23

##### Preparation of a polyester

35 [0102] A reaction vessel equipped with a refining distillation column was charged with 194 parts by weight of dimethyl terephthalate, 124 parts by weight of ethyleneglycol and 0.12 part by weight of calcium acetate; the charged mixture was subjected to an interesterification reaction at a temperature of 220°C; after the resultant methyl alcohol in a theoretical quantity was removed by evaporation, the reaction mixture was added with 0.09 part by weight of phosphoric acid, to complete a first stage of reaction. Then the above-mentioned reaction mixture was placed in a polymerization flask equipped with a refining distillation column, and mixed with a polymerization catalyst consisting of the catalyst (G) solution in an amount of 3.2 parts by weight (corresponding to a molar amount of titanium atoms of  $20 \times 10^{-3}$ %, based on the molar amount of dimethyl terephthalate) and a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 285°C under the ambient atmospheric pressure for 30 minutes and further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa (30 mmHg) for 15 minutes to proceed the reaction; and after the inside pressure of the reaction system was gradually reduced, and the reaction system was still further heated at the above-mentioned temperature for 110 minutes while the reaction system is agitated to complete the reaction. In the flask, the final inside temperature was 285°C and the final inside pressure was 49.3 Pa (0.37 mmHg).

45 [0103] The resultant polyethylene terephthalate had an intrinsic viscosity of 0.640. The test results of the polyester are shown in Table 3.

Example 24Preparation of a polyester

5 [0104] A polyester was prepared by the same procedures as in Example 23, except that as a polymerization catalyst, the catalyst (H) solution was employed.

[0105] The test results are shown in Table 3.

Table 3

Item	Catalyst		Properties of polyester					Height of foreign matter layer adhered around melt-spinning orifice (μm)	
	P/Ti molar ratio	Amount of catalyst (x <sup>-3</sup> g)	Intrinsic viscosity (dl/g)	Color tone L	Breakage number of backbone chains (eq./1,000 kg)	The number of foreign particles (particles/g)			
Example No.	17	2.0	20	0.640	85.5	1.8	3.1	320	4
	18	1.0	20	0.640	85.2	2.2	3.4	320	5
	19	3.0	20	0.640	86.2	2.2	2.8	350	7
	20	2.0	10	0.641	84.4	2.2	2.5	300	7
	21	2.0	30	0.640	85.2	2.9	3.7	380	8
	22	2.0	20	0.639	84.9	3.8	3.0	350	8
	23	2.0	20	0.640	84.4	4.1	3.8	400	9
	24	2.0	20	0.640	84.1	4.0	4.0	400	10
Comparative Example	13	0.5	20	0.640	84.2	7.9	5.3	410	10
	14	3.5	20	Reaction was not effected.					
	15	2.0	5	Reaction was not effected.					
	16	2.0	45	0.640	83.0	7.4	5.1	570	11

Example 25Preparation of catalyst (I)

40 [0106] Trimethyleneglycol in an amount of 2.5 parts by weight was dissolved in 0.8 part by weight of trimellitic anhydride and, into the resultant solution, titanium tetrabutoxide in an amount of 0.7 part by weight (corresponding to 0.5 molar% based on the molar amount of trimellitic anhydride) was added dropwise, the resultant reaction system was maintained at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. Thereafter, the reaction system was cooled to room temperature, and was mixed with 15 parts by weight of acetone, the resultant precipitation was collected by filtration through a No. 5 filter paper and dried at a temperature of 100°C for 2 hours. The resultant reaction product (titanium compound (2)) had a titanium content of 11.5% by weight.

45 [0107] Then, 3.6 parts by weight of phenylphosphinic acid were dissolved in 131 parts by weight of trimethyleneglycol by heating at a temperature of 120°C for 10 minutes. The resultant trimethyleneglycol solution in an amount of 134.5 parts by weight was further added with 40 parts by weight of trimethyleneglycol and, in the resultant solution, 5.0 parts by weight of the above-mentioned titanium compound (2) were dissolved. The resultant reaction system was heated and agitated at a temperature of 120°C for 60 minutes to produce a reaction product of the titanium compound (2) with phenylphosphinic acid. A white-colored slurry of a reaction product, namely a catalyst (I) was obtained. The slurry of the catalyst (I) had a titanium content of 0.3% by weight.

Preparation of a polyester

55 [0108] Terephthalic acid in an amount of 166 parts by weight and trimethyleneglycol in an amount of 92 parts by

5 weight were subjected to an esterification reaction with each other at a temperature of 240°C, the resultant reaction product was placed in a polymerization flask equipped with a refining distillation column, and was mixed with the slurry of catalyst (I) used, as a polymerization catalyst, in an amount of 0.95 parts by weight (corresponding to a molar amount of titanium atoms of  $20 \times 10^{-3}\%$  based on the molar amount of terephthalic acid) and with a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 250°C under the ambient atmospheric pressure for 30 minutes; further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa for 15 minutes; and still further heated at the above-mentioned temperature for 110 minutes while the reaction pressure was gradually reduced and the reaction system was agitated, to complete the reaction. When the reaction was completed, the inside temperature of the flask was 250°C and the 10 final reaction pressure was 49.3 Pa. The resultant polytrimethylene terephthalate had an intrinsic viscosity of 0.680.

[0109] The test results are shown in Table 4.

Examples 26 to 30 and Comparative Examples 17 to 20

15 [0110] In each of Examples 26 to 30 and Comparative Examples 17 to 20, a polyester was prepared by the same procedures as in Example 25, except that the P/Ti molar ratio of the catalyst (I), and the amount of the catalyst used in the polyester production were changed to those as shown in Table 4. The test results are shown in Table 4.

Example 31

20 Preparation of catalyst (J)

25 [0111] A mixture of 153 parts by weight of trimethyleneglycol with 5.0 parts by weight of phenylphosphinic acid was heated at 120°C for 10 minutes to provide a solution. Into 158.0 parts by weight of the ethyleneglycol solution, 3.4 parts by weight of titanium tetrabutoxide were added dropwise, and the resultant reaction system was agitated and heated at a temperature of 120°C for 60 minutes to react phenylphosphinic acid with titanium tetrabutoxide. A white-colored slurry containing the reaction product, namely a catalyst J was obtained. The catalyst (J) slurry had a titanium content of 0.3% by weight.

30 Preparation of a polyester

[0112] A polyester was prepared by the same procedures as in Example 25, except that the catalyst (J) was employed as the polymerization catalyst. The test results are shown in Table 4.

35 Example 32

Preparation of a polyester

40 [0113] A reaction vessel equipped with a refining distillation column was charged with 194 parts by weight of dimethyl terephthalate, 152 parts by weight of trimethyleneglycol and 0.12 part by weight of calcium acetate; the charged mixture was subjected to an interesterification reaction at a temperature of 220°C; after the resultant methyl alcohol in a theoretical quantity was removed by evaporation, the reaction mixture was added with 0.09 part by weight of phosphoric acid, to complete a first stage of reaction. Then the above-mentioned reaction mixture was placed in a polymerization flask equipped with a refining distillation column, and mixed with a polymerization catalyst consisting of the catalyst (I) slurry in an amount of 3.2 parts by weight (corresponding to a molar amount of titanium atoms of  $20 \times 10^{-3}\%$  based on the molar amount of dimethyl terephthalate) and a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 250°C under the ambient atmospheric pressure for 30 minutes and further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa for 15 minutes to proceed the reaction; and after the inside pressure of the reaction system was gradually reduced, and the reaction system was still further heated at the above-mentioned temperature for 110 minutes while agitating the reaction system, to complete the reaction. In the flask, the final inside temperature was 250°C and the final inside pressure was 49.3 Pa (0.37 mmHg).

45 [0114] The resultant polytrimethylene terephthalate had an intrinsic viscosity of 0.678. The test results of the polyester are shown in Table 4.

Example 33Preparation of a polyester

5 [0115] A polyester was prepared by the same procedures as in Example 33, except that the catalyst (J) was employed as the polymerization catalyst. The results are shown in Table 4.

Comparative Example 21

10 [0116] A polyester was prepared by the same procedures as in Example 32, except that, as a polymerization catalyst, titanium tetrabutoxide was employed, and the catalyst content and the amount of the catalyst slurry was controlled so that the amount of this catalyst in terms of molar amount of titanium atoms is  $20 \times 10^{-3}\%$  based on the molar amount of dimethyl terephthalate. The test results are shown in Table 4.

15 Example 34Preparation of catalyst (K)

20 [0117] Tetramethyleneglycol in an amount of 2.5 parts by weight was dissolved in 0.8 part by weight of trimellitic anhydride and, into the resultant solution, titanium tetrabutoxide in an amount of 0.7 part by weight (corresponding to 0.5 molar% based on the molar amount of trimellitic anhydride) was added dropwise and the resultant reaction system was maintained at a temperature of 80°C for 60 minutes to react titanium tetrabutoxide with trimellitic anhydride and to age the reaction product. Thereafter, the reaction system was cooled to room temperature, and was mixed with 15 parts by weight of acetone, the resultant precipitation was collected by filtration through a No. 5 filter paper and dried at a temperature of 100°C for 2 hours. The resultant reaction product (titanium compound (2)) had a titanium content of 11.5% by weight.

25 [0118] Then, 3.6 parts by weight of phenylphosphonic acid were dissolved in 131 parts by weight of tetramethyleneglycol by heating at a temperature of 120°C for 10 minutes. The resultant tetramethyleneglycol solution in an amount of 134.5 parts by weight was further added with 40 parts by weight of tetramethyleneglycol, and in the resultant solution, 30 5.0 parts by weight of the above-mentioned titanium compound (2) were dissolved. The resultant reaction system was agitated and heated at a temperature of 120°C for 60 minutes. A white-colored slurry containing a catalyst (K) was obtained. The slurry of the catalyst (K) had a titanium content of 0.3% by weight.

Preparation of a polyester

35 [0119] Terephthalic acid in an amount of 166 parts by weight and tetramethyleneglycol in an amount of 109 parts by weight were subjected to an esterification reaction with each other at a temperature of 240°C, the resultant reaction product was placed in a polymerization flask equipped with a refining distillation column, and was mixed with the slurry of catalyst (K) as a polymerization catalyst, in an amount of 0.95 parts by weight (corresponding to a molar amount of 40 titanium atoms of  $20 \times 10^{-3}\%$  based on the molar amount of terephthalic acid) and with a color tone-regulating agent consisting of TERAZOLE BLUE in an amount of 0.0002 part by weight. The resultant reaction system was heated to a temperature of 250°C under the ambient atmospheric pressure for 30 minutes; further heated at the above-mentioned temperature under a reduced pressure of 4.0 kPa for 15 minutes; and still further heated at the above-mentioned temperature for 110 minutes while the reaction pressure was gradually reduced and the reaction system was agitated, 45 to complete the reaction. When the reaction was completed, the inside temperature of the flask was 250°C and the final reaction pressure was 49.3 Pa. The resultant polytetramethylene terephthalate had an intrinsic viscosity of 0.700.

[0120] The test results are shown in Table 4.

Comparative Example 22

50 [0121] A polyester was prepared by the same procedures as in Example 25, except that, as a polymerization catalyst, the catalyst (C) mentioned in Comparative Example 6 was employed above, and the catalyst content and the amount of the catalyst slurry was controlled so that the amount of this catalyst in terms of molar amount of titanium atoms was  $20 \times 10^{-3}\%$  based on the molar amount of terephthalic acid. The test results are shown in Table 4.

Comparative Example 23Preparation of a catalyst (L)

5 [0122] A catalyst was prepared by the same procedures as in Example 25, except that 3.6 parts by weight of phenyl phosphite were employed in place of 3.6 parts by weight of phenylphosphonic acid. A white colored slurry containing a catalyst (L) was obtained. The catalyst (L) slurry has a titanium content of 0.3% by weight.

Preparation of a polyester

10 [0123] A polyester was prepared by the same procedures as in Example 25, except that as a polymerization catalyst, the catalyst (L) slurry was employed in an amount of 3.2 parts by weight corresponding a molar amount of titanium atoms of  $20 \times 10^{-3}\%$  based on the molar amount of terephthalic acid. The test results are shown in Table 4.

Comparative Example 24

15 [0124] A polyester was prepared by the same procedures as in Example 32, except that, as a polymerization catalyst, diantimony trioxide was employed alone, and the amount of the catalyst was controlled to a molar amount in terms of titanium atoms of  $20 \times 10^{-3}\%$  based on the molar amount of terephthalic acid. The test results are shown in Table 4.

20

Table 4

25	Item	Catalyst		Properties of polyester				Height of foreign matter layer adhered around melt- spinning orifice ( $\mu\text{m}$ )		
		P/Ti molar ratio	Amount of catalyst ( $\text{x}^{-3}\%$ )	Intrin- sic vis- cosity (dl/g)	Color tone L	Breakage number of backbone chains b	The number of foreign particles ( $\text{eq.}/$ 1,000 kg) ( $\text{g}$ )			
30	Example No.	25	2.0	20	0.680	88.0	1.2	2.7	290	7
		26	1.0	20	0.679	87.2	1.5	3.2	310	8
		27	3.0	20	0.681	88.2	0.9	2.4	340	5
		28	2.0	10	0.680	87.3	1.8	2.5	280	8
		29	2.0	30	0.680	87.2	2.0	3.7	370	9
		30	2.0	20	0.679	86.5	3.0	2.9	350	7
		31	2.0	20	0.678	87.0	3.2	3.5	400	8
		32	2.0	20	0.680	87.1	3.8	3.8	400	7
		33	2.0	20	0.700	89.0	1.1	2.9	290	6
		17	0.5	20	0.680	85.1	7.9	5.6	450	12
35	Compar- ative Example	18	3.5	20	Reaction was not effected.					
		19	2.0	5	Reaction was not effected.					
		20	2.0	45	0.679	83.8	7.5	4.9	560	15
		21	-	20	0.680	82.3	9.9	5.9	730	7
		22	-	20	0.681	84.0	6.2	5.3	580	9
		23	2.0	20	0.680	84.2	6.8	3.6	550	10
		24	( $\text{Sb}_2\text{O}_3$ )	25	0.679	84.4	0.5	3.5	380	52

## INDUSTRIAL APPLICABILITY

55

[0125] By using the catalyst of the present invention and the process for producing a polyester using the catalyst, a polyester having an excellent color tone, a small content of foreign matter and an excellent melting heat stability can be produced. Further, the polyester obtained in accordance with the process of the present invention is advantageous

in that even when the melt-spinning procedure for the polyester is continuously carried out through a melt-spinning orifice over a long period, a foreign matter is adhered in a very small amount to around the melt spinning orifice, and the polyester exhibits an excellent forming property.

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### Claims

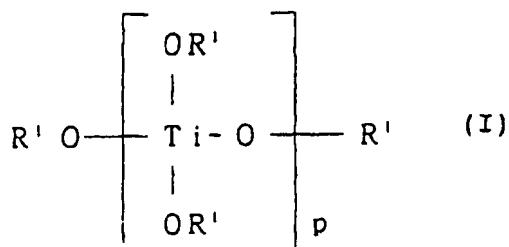
1. A catalyst for producing a polyester comprising a reaction product of

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(A) a titanium compound component comprising at least one member selected from the group consisting of:

titanium compounds (1) represented by the general formula (I):

15



20

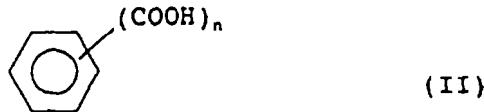
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in which formula (I), R<sup>1</sup> represents an alkyl group having 2 to 10 carbon atoms and p represents an integer of 1 to 3, and

titanium compounds (2) produced by reacting the titanium compounds (1) of the formula (I) with aromatic polycarboxylic acids represented by the general formula (II):

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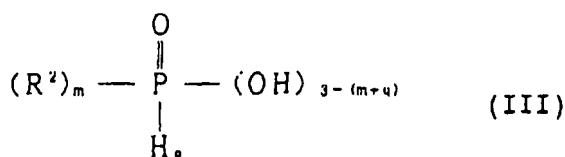


in which formula (II), n represents an integer of 2 to 4, or anhydrides of the aromatic polycarboxylic acids of the formula (II), with

40

(B) a phosphorus compound component comprising at least one member selected from the phosphorus compounds (3) of the general formula (III):

45



50

in which formula (III), m represents an integer of 1 or 2, q represents an integer of 0 or 1, the sum of m and q is 1 or 2, R<sup>2</sup> represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms or alkyl group having 1 to 20 carbon atoms and when m represent 2, the two R<sup>2</sup> groups are the same as each other or different from each other.

55

2. The catalyst for producing a polyester as claimed in claim 1, wherein in the reaction product of the titanium compound component (A) with the phosphorus compound component (B), a ratio of the amount of the titanium compound component (A) in terms of a molar amount of titanium atoms (m<sub>Ti</sub>) to the amount of the phosphorus com-

pound component (B) in terms of a molar amount of phosphorus atoms ( $m_p$ ) is in the range of from 1:1 to 1:4.

3. The catalyst for producing a polyester as claimed in claim 1, wherein the titanium compound (1) of the formula (I) is selected from the group consisting of titanium tetraalkoxides, octaalkyl tritanates and hexaalkyl dititanates.

5

4. The catalyst for producing a polyester as claimed in claim 1, wherein the aromatic polycarboxylic acids of the formula (II) or anhydrides thereof are selected from the group consisting of phthalic acid, trimellitic acid, hemimellitic acid and pyromellitic acid or anhydrides of the above-mentioned acids.

10

5. The catalyst for producing a polyester as claimed in claim 1, wherein the titanium compounds (2) are reaction products of the titanium compounds (1) of the formula (I) with the aromatic polycarboxylic acids of the formula (II) or the anhydrides thereof in a reaction molar ratio of 2:1 to 2:5.

15

6. The catalyst for producing a polyester as claimed in claim 1, wherein the phosphorus compounds (3) of the formula (III) are selected from the group consisting of: phenylphosphonic acid, methylphosphonic acid, ethylphosphonic acid, propylphosphonic acid, isopropylphosphonic acid, butylphosphonic acid, tolylphosphonic acid, xylylphosphonic acid, biphenylphosphonic acid, naphthylphosphonic acid, anthrylphosphonic acid, 2-carboxyphenylphosphonic acid, 3-carboxyphenylphosphonic acid, 4-carboxyphenylphosphonic acid, 2,3-dicarboxyphenylphosphonic acid, 2,4-dicarboxyphenylphosphonic acid, 2,5-dicarboxyphenylphosphonic acid, 2,6-dicarboxyphenylphosphonic acid, 3,4-dicarboxyphenylphosphonic acid, 3,5-dicarboxyphenylphosphonic acid, 2,3,4-tricarboxyphenylphosphonic acid, 2,3,5-tricarboxyphenylphosphonic acid, 2,3,6-tricarboxyphenylphosphonic acid, 2,4,5-tricarboxyphenylphosphonic acid, 2,4,6-tricarboxyphenylphosphonic acid, phenylphosphinic acid, methylphosphinic acid, ethylphosphinic acid, propylphosphinic acid, isopropylphosphinic acid, butylphosphinic acid, tolylphosphinic acid, xylylphosphinic acid, biphenylphosphinic acid, diphenylphosphinic acid, dimethylphosphinic acid, diethylphosphinic acid, dipropylphosphinic acid, diisopropylphosphinic acid, dibutylphosphinic acid, ditolylphosphinic acid, dixylylphosphinic acid, dibiphenylphosphinic acid, naphthylphosphinic acid, anthrilphosphinic acid, 2-carboxyphenylphosphinic acid, 3-carboxyphenylphosphinic acid, 4-carboxyphenylphosphinic acid, 2,3-dicarboxyphenylphosphinic acid, 2,4-dicarboxyphenylphosphinic acid, 2,5-dicarboxyphenylphosphinic acid, 2,6-dicarboxyphenylphosphinic acid, 3,4-dicarboxyphenylphosphinic acid, 3,5-dicarboxyphenylphosphinic acid, 2,3,4-tricarboxyphenylphosphinic acid, 2,3,5-tricarboxyphenylphosphinic acid, 2,3,6-tricarboxyphenylphosphinic acid, 2,4,5-tricarboxyphenylphosphinic acid, 2,4,6-tricarboxyphenylphosphinic acid, bis(2-carboxyphenyl)phosphinic acid, bis(3-carboxyphenyl)phosphinic acid, bis(4-carboxyphenyl)phosphinic acid, bis(2,3-dicarboxyphenyl)phosphinic acid, bis(2,4-dicarboxyphenyl)phosphinic acid, bis(2,5-dicarboxyphenyl)phosphinic acid, bis(2,6-dicarboxyphenyl)phosphinic acid, bis(3,4-dicarboxyphenyl)phosphinic acid, bis(3,5-dicarboxyphenyl)phosphinic acid, bis(2,3,4-tricarboxyphenyl)phosphinic acid, bis(2,3,5-tricarboxyphenyl)phosphinic acid, bis(2,3,6-tricarboxyphenyl)phosphinic acid, bis(2,4,5-tricarboxyphenyl)phosphinic acid, and bis(2,4,6-tricarboxyphenyl)phosphinic acid.

7. The catalyst for producing a polyester as claimed in claim 1; wherein the reaction product of the titanium compound component (A) with the phosphorus compound component (B) is one produced at a reaction temperature of 0 to 40 200°C.

8. A process for producing a polyester comprising a step of polymerizing a polymerization-starting material comprising at least one member selected from the group consisting of alkylene glycol esters of aromatic difunctional carboxylic acids and oligomers thereof in the presence of a catalyst, wherein the catalyst comprises a reaction product of

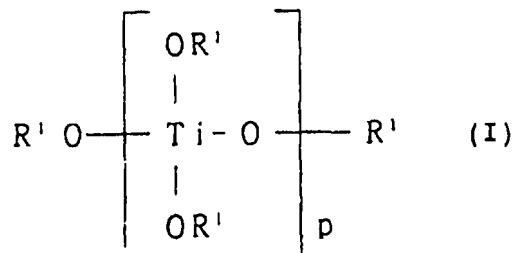
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(A) a titanium compound component comprising at least one member selected from the group consisting of:

titanium compounds (1) represent by the general formula (I):

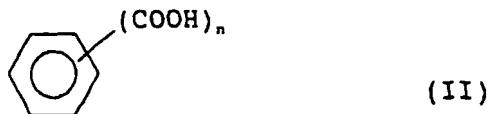
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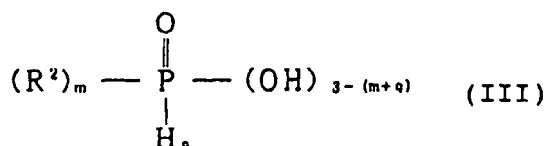
in which formula (I),  $\text{R}^1$  represents an alkyl group having 2 to 10 carbon atoms and  $p$  represents an integer of 1 to 3, and

15 titanium compounds (2) produced by reacting the titanium compounds (1) of the formula (I) with aromatic polycarboxylic acids represented by the general formula (II):



25 in which formula (II),  $n$  represents an integer of 2 to 4, or anhydrides of the aromatic polycarboxylic acids of the formula (II), with

30 (B) a phosphorus compound component comprising at least one member selected from the phosphorus compounds (3) of the general formula (III):



40 in which formula (III),  $m$  represents an integer of 1 or 2,  $q$  represents an integer of 0 or 1, the sum of  $m$  and  $q$  is 1 or 2,  $\text{R}^2$  represents an unsubstituted or substituted aryl group having 6 to 20 carbon atoms or alkyl group having 1 to 20 carbon atoms, and when  $m$  represent 2, the two  $\text{R}^2$  groups are the same as each other or different from each other, and the amount of the catalyst in terms of molar amount in millimole of titanium atoms contained in the catalyst in corresponds to 10 to 40% of the amount in millimole of the aromatic difunctional carboxylic acid contained in the polymerization-starting material.

45 9. The process for producing a polyester as claimed in claim 8, wherein in the reaction product of the titanium compound component (A) with the phosphorus compound component (B), a ratio of the amount of the titanium compound component (A) in terms of molar amount of titanium atoms ( $m_{\text{Ti}}$ ) to the amount of the phosphorus compound component (B) in terms of molar amount of phosphorus atoms ( $m_p$ ) is in the range of from 1:1 to 1:4.

50 10. The process for producing a polyester as claimed in claim 8, wherein the aromatic difunctional acid is selected from the group consisting of terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, biphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyletherdicarboxylic acid, diphenoxethanedicarboxylic acid, and  $\beta$ -hydroethoxybenzoic acid.

55 11. The process for producing a polyester as claimed in claim 8, wherein the alkyleneglycols are selected from ethyleneglycol, trimethyleneglycol, tetramethyleneglycol, neopentylglycol and hexamethyleneglycol.

12. The process for producing a polyester as claimed in claim 8, wherein the polymerization reaction is carried out at a temperature of 230 to 320°C.

13. A polyester produced by the process as claimed in any of claims 8 to 12.

5 14. The polyester as claimed in claim 13, which contains no cobalt compound and satisfies the requirement that:

(a) when the polyester is melted at a temperature of 290°C under vacuum for 10 minutes, the melt is formed into a plate having a thickness of  $3.0 \pm 1$  mm on an aluminum plate, immediately after the forming, the polyester plate is rapidly cooled in ice water, and then is dried and subjected to a crystallization treatment at a temperature of 160°C for one hour, then the crystallized polyester plate is placed on a plate having a standard whiteness for tuning a color difference meter, and the color tone of the polyester plate surface is measured by using the color difference meter, the L value of the polyester plate surface is 80.0 or more and the b value of the polyester plate surface is in the range of from -2.0 to 5.0.

15 15. The polyester as claimed in claim 13, satisfying the requirement that:

(b) the content of solid foreign particles having an average particle size of 3  $\mu\text{m}$  or more is limited to 500 particles/g or less.

16. The polyester as claimed in claim 13, satisfying the requirement that:

20 (c) when heated in a nitrogen gas atmosphere at a temperature of 290°C for 15 minutes, the number of breakage of backbone chains of the polyester molecules is 4.0 equivalents/1,000 kg or less.

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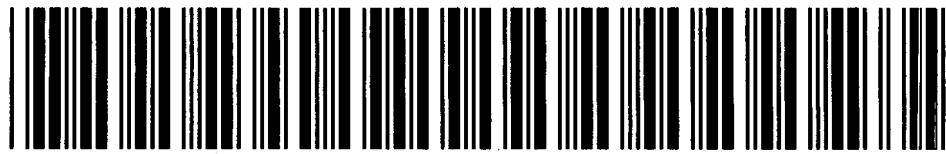
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INTERNATIONAL SEARCH REPORT		International application No. PCT/JP00/04159
A. CLASSIFICATION OF SUBJECT MATTER Int.Cl <sup>7</sup> C08G63/82		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> C08G63/00-63/91		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-2000 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, 5453479, A (General Electric Company), 26 September, 1995 (26.09.95), Column 9, line 66 to Column 12, line 5 & JP, 7-138354, A page 2, left column, lines 2 to 27 & EP, 634435, A1	1-16
A	JP, 4-189821, A (Toray Industries, Inc.), 08 July, 1992 (08.07.92), page 1, lower left column, lines 5 to 19; page 4, upper right column, lines 3 to 13; page 4, lower left column, lines 8 to 19	1-16
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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# IDS REFERENCES



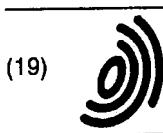
FOR

EP1273610

**Title:**  
**POLYESTER RESIN AND METHOD FOR PRODUCTION THEREOF**

**Abstract:**

A polyester resin, whereby a molded product excellent in a gas barrier property and also excellent in an ultraviolet shielding property, a color tone, etc., and which is particularly suitable for molding a bottle for e.g. a beverage required to have an aroma retention property, and further, a polyester resin, whereby the acetaldehyde content as a molded product is reduced to eliminate an influence over the taste, aroma, etc. of the content, and a process for its production, wherein the polycondensability is improved, are to be presented. A polyester resin produced by polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, via an esterification reaction or an ester exchange reaction, characterized in that the content of copolymerized components other than the terephthalic acid component and the ethylene glycol component, is not more than 4 mol% based on the total dicarboxylic acid component, and in a molded product with a thickness of 3.5 mm injection-molded at 280 DEG C, the difference between the absorbance at a wavelength of 395 nm and the absorbance at a wavelength of 800 nm is at least 0.08, and the difference between the absorbance at a wavelength of 500 nm and the absorbance at a wavelength of 800 nm is at most 0.05; and a process for producing a polyester resin, which comprises polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) a compound of at least one element selected from the group consisting of metal elements of Group 1a of the periodic table, elements of Group 1Ia of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, via an esterification reaction or an ester exchange reaction, characterized in that the amounts of the respective compounds (1), (2) and (3) are such amounts that their contents will be from 0.02 to 0.2 mol as the total amount (T) of atoms of the compound (1), from 0.04 to 0.6 mol as the total amount (M) of atoms of the compound (2) and from 0.02 to 0.4 mol as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin.



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**(54) POLYESTER RESIN AND METHOD FOR PRODUCTION THEREOF**

(57) A polyester resin, whereby a molded product excellent in a gas barrier property and also excellent in an ultraviolet shielding property, a color tone, etc., and which is particularly suitable for molding a bottle for e.g. a beverage required to have an aroma retention property, and further, a polyester resin, whereby the acetaldehyde content as a molded product is reduced to eliminate an influence over the taste, aroma, etc. of the content, and a process for its production, wherein the polycondensability is improved, are to be presented.

A polyester resin produced by polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, via an esterification reaction or an ester exchange reaction, characterized in that the content of copolymerized components other than the terephthalic acid component and the ethylene glycol component, is not more than 4 mol% based on the total dicarboxylic acid component, and in a molded product with a thickness of 3.5 mm injection-molded at 280°C, the difference between the absorbance at a wavelength of 395 nm and

the absorbance at a wavelength of 800 nm is at least 0.08, and the difference between the absorbance at a wavelength of 500 nm and the absorbance at a wavelength of 800 nm is at most 0.05; and a process for producing a polyester resin, which comprises polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) a compound of at least one element selected from the group consisting of metal elements of Group 1a of the periodic table, elements of Group 11a of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, via an esterification reaction or an ester exchange reaction, characterized in that the amounts of the respective compounds (1), (2) and (3) are such amounts that their contents will be from 0.02 to 0.2 mol as the total amount (T) of atoms of the compound (1), from 0.04 to 0.6 mol as the total amount (M) of atoms of the compound (2) and from 0.02 to 0.4 mol as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin.

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**Description****TECHNICAL FIELD**

5 [0001] The present application claims a benefit of Japanese Patent Application No. 2001-29135, and the content of this application will be referred to as a reference in the present specification.

[0002] The present invention relates to a polyester resin, whereby a molded product excellent in a gas barrier property and also excellent in an ultraviolet shielding property, a color tone, etc., and which is particularly suitable for molding a bottle for e.g. a beverage required to have an aroma retention property, and further, to a polyester resin, whereby 10 the acetaldehyde content in a molded product is reduced to eliminate an influence over the taste, aroma, etc. of the content, and a process for its production, whereby the polycondensability is improved.

**BACKGROUND ART**

15 [0003] Heretofore, a polyester resin such as a polyethylene terephthalate resin has been widely used for packaging containers for various beverages, etc., since it is excellent in mechanical strength, chemical stability, gas barrier property, aroma-retention property, hygienics, etc., and is relatively inexpensive and light in weight. Especially, as a container for a beverage which requires heat sterilization filling, for e.g. a fruit juice beverage, a bottle having a high gas barrier property, etc. imparted by an application of stretch heat setting, has shown a rapid expansion. Such a bottle is produced, 20 for example, by injection molding a bottomed tubular preform, reheating the preform to soften it, followed by stretch blow molding. At that time, the blow mold is heated to apply heat setting to the bottle, whereby crystals of molecular chains aligned by stretching are fixed to provide the high gas barrier property, etc.

[0004] However, with respect to the polyethylene terephthalate resin to be used in such a field of beverage containers, 25 in the case of a polyethylene terephthalate resin produced by using an antimony compound as a polycondensation catalyst, which is most commonly used for bottles for wide range of purpose, copolymerizable components such as isophthalic acid, diethylene glycol, etc. other than the terephthalic acid component and the ethylene glycol component, are copolymerized in an amount of from about 3 to 10 mol% based on the total dicarboxylic acid component in order to provide transparency, whereby the intended gas barrier property may not be obtained, whereby the aroma-retention property as a bottle tends to decrease, and the aroma of the content is likely to decrease, or the ultraviolet shielding 30 property tends to be poor, whereby the flavor component or the color tone of the content is likely to deteriorate, and further, another problem is also worried such that antimony remaining in the resin will elute from the container at a high temperature and will transfer to the contained beverage although slightly. On the other hand, with a polyethylene terephthalate resin prepared by using a germanium compound as a polycondensation catalyst, which is commonly used for heat resistant bottles, copolymerizable components other than the terephthalic acid component and the ethylene glycol 35 component, may be copolymerized in a relatively small amount at a level of more than 2 to 5 mol% based on the total dicarboxylic acid component, but the above-mentioned problem relating to a decrease of the aroma-retention property cannot still be solved, and the ultraviolet shielding property is also inferior, and further, the germanium compound is expensive, whereby an economical disadvantage cannot be avoided. Accordingly, it is strongly desired to have a substitute polycondensation catalyst developed.

40 [0005] Further, many polyethylene terephthalate resins have been proposed which are prepared by using titanium compounds as polycondensation catalysts, but they have had problems such that they lack in thermal stability, so that the obtainable resins tend to have a yellowish color tone, or the change in the color tone after being heated is substantial, and further have problems such that acetaldehyde, a cyclic trimer, etc. are formed in a large amount as by-products 45 during the polycondensation and the melt molding, and when used as bottles, they tend to deteriorate the tastes, aromas, etc. of the contained beverages. Whereas, e.g. JP-A-8-73581 discloses a process for producing a polyethylene terephthalate resin which is colorless and excellent in transparency, by using a titanium compound, a cobalt compound, and a limited amount of complex-forming agent, such as phosphoric acid, phosphorous acid and/or phosphonic acid or its derivative. However, according to the study conducted by the present inventors, it has been found that the polyethylene terephthalate resin obtainable by this process is not one which is able to solve the above-mentioned problem 50 such as a decrease in the aroma-retention property and the problem such as deterioration of the taste, the aroma, etc. of the content.

[0006] Further, EP-A-1013692 discloses that production of acetaldehyde as a by-product during the polycondensation and the melt molding can be suppressed by using titanium and metal compounds, as polycondensation catalysts, so that specific amounts of titanium atoms and metal atoms such as magnesium, would be in a specific ratio. Further, 55 in JP-A-2000-339919 filed by the present applicants, it is disclosed that in the polycondensation in the presence of (1) a titanium compound, (2) a compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table and manganese, and (3) a phosphorus compound, the order of addition of the respective compounds (1), (2) and (3) is set to be (3), then (2) and then (1),

whereby by-products such as acetaldehyde, a cyclic trimer, etc., can be reduced. However, according to the study by the present inventors, it has been found that these methods are certainly effective to reduce by-products, but with the disclosed methods, there is still a room for improvement with respect to the gas barrier property, the ultraviolet shielding property or the polycondensability.

5 [0007] The present invention has been made in view of the above-described prior art, and it is an object of the present invention to provide a polyester resin, whereby a molded product excellent in the gas barrier property and also excellent in the ultraviolet shielding property, the color tone, etc., and which is particularly suitable for molding a bottle for e.g. a beverage required to have an aroma-retention property, and further, a polyester resin, whereby the acetaldehyde content as a molded product is reduced to eliminate an influence over the taste, the aroma, etc. of the content, and a process for its production, whereby the polycondensability is improved.

#### DISCLOSURE OF THE INVENTION

15 [0008] As its gist, the present invention provides a polyester resin produced by polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, via an esterification reaction or an ester exchange reaction, characterized in that the content of copolymerized components other than the terephthalic acid component and the ethylene glycol component, is not more than 4 mol% based on the total dicarboxylic acid component, and in a molded product with a thickness of 3.5 mm injection-molded at 280°C, the difference between the absorbance at a wavelength of 395 nm and the absorbance at a wavelength of 800 nm is at least 0.08, and the difference between the absorbance at a wavelength of 500 nm and the absorbance at a wavelength of 800 nm is at most 0.05.

20 [0009] Further, as its gist, the present invention provides a process for producing a polyester resin, which comprises polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) a compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, via an esterification reaction or an ester exchange reaction, characterized in that the amounts of the respective compounds (1), (2) and (3) are such amounts that their contents will be from 0.02 to 0.2 mol as the total amount (T) of atoms of the compound (1), from 0.04 to 0.6 mol as the total amount (M) of atoms of the compound (2) and from 0.02 to 0.4 mol as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin.

35 BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

40 Fig. 1(a): a plan view of a stepped molded plate for evaluation of the physical properties, molded in Examples.  
Fig. 1(b): a front view of the stepped molded plate for evaluation of the physical properties, molded in Examples.

BEST MODE FOR CARRYING OUT THE INVENTION

45 [0011] The polyester resin of the present invention is one produced by polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component, via an esterification reaction or an ester exchange reaction, and is preferably a polycondensate of a dicarboxylic acid component in which the terephthalic acid component constitutes at least 96 mol%, more preferably at least 99 mol%, of the total dicarboxylic acid component, with a diol component in which the ethylene glycol component constitutes at least 96 mol%, more preferably at least 97 mol%, of the total diol component.

50 If the proportion of the terephthalic acid component in the total dicarboxylic acid component, and the proportion of the ethylene glycol component in the total diol component, are less than the above ranges, the aligned crystallization of the molecular chains by stretching at the time of molding a bottle, etc., tends to be inadequate, whereby the mechanical strength, the gas barrier property, the heat resistance, etc., as a molded product such as a bottle, tend to be inadequate.

55 [0012] And, in the polyester resin of the present invention, it is essential that the content of copolymerizable components other than the terephthalic acid component and the ethylene glycol component is not more than 4 mol%, preferably not more than 3 mol%, further preferably not more than 2 mol%. If the content of copolymerizable components exceeds the above range, it tends to be difficult to obtain a molded product which is excellent in e.g. the aroma-retention property, etc., and in which the acetaldehyde content is reduced.

[0013] Further, the ester-forming derivative of terephthalic acid may, for example, be a C<sub>1-4</sub> alkyl ester, a halogenated product, etc. Further, dicarboxylic acid components other than terephthalic acid or its ester-forming derivative, may, for example, be an aromatic dicarboxylic acid such as phthalic acid, isophthalic acid, dibromoisophthalic acid, sodium sulfoisophthalate, phenylene dioxydicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, 4,4'-diphenyl ketone dicarboxylic acid, 4,4'-diphenoxymethane dicarboxylic acid, 4,4'-diphenylsulfone dicarboxylic acid or 2,6-naphthalene dicarboxylic acid, an alicyclic dicarboxylic acid such as hexahydroterephthalic acid or hexahydroisophthalic acid, and an aliphatic dicarboxylic acid such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebatic acid, undecadicarboxylic acid or dodecacarboxylic acid, as well as a C<sub>1-4</sub> alkyl ester thereof, and a halogenated product thereof. Among them, in the present invention, isophthalic acid or its ester-forming derivative is preferred, and the proportion in the total dicarboxylic acid component is preferably from 0.1 to 3 mol%. If isophthalic acid is within this range, the solid phase polycondensation rate is high, and reduction of the acetaldehyde content in a molded product of the obtainable resin tends to be facilitated.

[0014] Further, as the diol component other than ethylene glycol, diethylene glycol formed as a by-product in the reaction system may be mentioned, and the proportion of such diethylene glycol in the total diol component is preferably not more than 3 mol%, more preferably from 1 to 3 mol%, inclusive of one added as a copolymerizable component from outside the system. If diethylene glycol exceeds this range, a problem tends to occur such that when the obtainable resin is formed into a molded product, the gas barrier property decreases, or it tends to be difficult to reduce the acetaldehyde content. Further, other diol components may, for example, be an aliphatic diol such as trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, octamethylene glycol, decamethylene glycol, neopentyl glycol, 2-ethyl-2-butyl-1,3-propane diol, polyethylene glycol or polytetramethylene ether glycol, an alicyclic diol such as 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,1-cyclohexanedimethylol, 1,4-cyclohexanedimethylol or 2,5-norbornanedimethylol, and an aromatic diol such as xylylene glycol, 4,4'-dihydroxybiphenyl, 2,2-bis(4'-hydroxyphenyl)propane, 2,2-bis(4'-β-hydroxyethoxyphenyl)propane, bis(4-hydroxyphenyl)sulfone or bis(4-β-hydroxyethoxyphenyl)sulfonic acid, as well as an ethylene oxide adduct or a propylene oxide adduct, of 2,2-bis(4'-hydroxyphenyl)propane.

[0015] Further, copolymerizable components may, for example, be a hydroxycarboxylic acid or an alkoxy carboxylic acid, such as glycolic acid, p-hydroxybenzoic acid or p-β-hydroxyethoxybenzoic acid, a single functional component such as stearyl alcohol, heptycosanol, octacosanol, benzyl alcohol, stearic acid, behenic acid, benzoic acid, t-butyl benzoic acid or benzoylbenzoic acid, and a polyfunctional component with at least trifunctional, such as tricarbaryllic acid, trimellitic acid, trimesic acid, pyromellitic acid, naphthalene tetracarboxylic acid, gallic acid, trimethylethane, trimethylolpropane, glycerol, pentaerythritol or sugar ester.

[0016] The polyester resin of the present invention is such that in a molded product with a thickness of 3.5 mm injection-molded at 280°C, the difference between the absorbance at a wavelength of 395 nm and the absorbance at a wavelength of 800 nm is at least 0.08, and this difference in absorbance is preferably at least 0.15, more preferably at least 0.20. If this difference in absorbance is less than the above range, it tends to be difficult to obtain a molded product excellent in the ultraviolet shielding property. Further, in a molded product having a thickness of 3.5 mm injection-molded at 280°C, the difference between the absorbance at a wavelength of 500 nm and the absorbance at a wavelength of 800 nm is at most 0.05, and this difference in absorbance is preferably at most 0.04, more preferably at most 0.03. If this difference in absorbance is less than the above range, it tends to be difficult to obtain a molded product excellent in the color tone. Here, the absorbance of a molded product is a value at each wavelength when measured by means of an ultraviolet visible light absorption photometer within a wavelength range of from 300 to 800 nm at a scanning speed of 127 nm/min.

[0017] Further, the polyester resin of the present invention is such that the temperature-rising crystallization temperature (Tc) of the resin in the molded product after the injection molding at 280°C, is preferably from 150 to 180°C, more preferably from 155 to 165°C, particularly preferably from 157 to 164°C. This temperature-rising crystallization temperature (Tc) relates to the crystallization rate of the mouth stopper portion, etc. at the time of molding a bottle, and if the temperature-rising crystallization temperature (Tc) is either less than the above range or more than the above range, the dimensional stability at the mouth stopper portion deteriorates as a bottle, and a problem such as leakage of a gas from the mouth stopper portion or deterioration of the aroma-retention property, tends to result. Here, the temperature-rising crystallization temperature (Tc) is one obtained by measuring the crystallization peak temperature observed in the temperature rise when the temperature was raised from 20°C to 285°C at a rate of 20°C/min in a nitrogen stream by means of a differential scanning calorimeter.

[0018] Further, the polyester resin of the present invention is such that the intrinsic viscosity ([η]) is preferably from 0.70 to 0.90 dL/g, more preferably from 0.70 to 0.80 dL/g, as a value measured at 30°C in a solution in a mixed solvent of phenol/tetrachloroethane (weight ratio: 1/1). If the intrinsic viscosity ([η]) is less than the above range, the mechanical strength tends to be inadequate as a molded product such as a bottle. On the other hand, if it exceeds the above range, the moldability for a bottle or the like tends to deteriorate, and it tends to be difficult to control production of acetaldehyde, etc. as by-products at the time of the melt molding. Further, as the color tone, the color coordinate value b of the

Hunter's color difference formula in the Lab color system as disclosed in Reference 1 in JIS Z8730, is preferably not more than 4, more preferably from -5 to 2. If value b exceeds the above range, the color tone tends to be yellowish as a molded product such as a bottle. Further, the cyclic trimer content (CT) is preferably not more than 0.50 wt%, more preferably not more than 0.40 wt%. If the cyclic trimer content (CT) exceeds the above range, contamination of the mold tends to occur during molding of a bottle, etc.

5 [0019] Further, the acetaldehyde content (AA<sub>1</sub>) is preferably not more than 5.0 ppm, more preferably not more than 3.0 ppm. Further, the acetaldehyde content (AA<sub>2</sub>) of the resin in a molded product after injection-molded at 280°C, is preferably not more than 20 ppm, more preferably not more than 18 ppm, particularly preferably not more than 15 ppm. If the acetaldehyde content (AA<sub>1</sub>) and the acetaldehyde content (AA<sub>2</sub>) exceed the above ranges, it tends to be difficult 10 to eliminate an influence over the taste, the aroma, etc. of the content, as a molded product such as bottle. Further, the haze of a molded product with a thickness of 5 mm after the injection molding at 280°C is preferably not more than 10%, more preferably not more than 8%.

15 [0020] And, in the present invention, in order to bring the above-mentioned content of copolymerizable components, the intrinsic viscosity ([η]), color coordinate value b, the cyclic trimer content (CT), the acetaldehyde content (AA<sub>1</sub>), as well as the absorbance of the molded product after the injection molding at 280°C, the temperature-rising crystallization 20 temperature (Tc), the acetaldehyde content (AA<sub>2</sub>), and the haze, etc. within the above ranges, it is essential that the polycondensation of the polyester resin is carried out in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table. Accordingly, the polyester resin of the present invention contains (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table.

25 [0021] Here, (1) the compound of a titanium group element of Group 4A of the periodic table, i.e. titanium, zirconium or hafnium, may, for example, be an oxide, a hydroxide, an alkoxide, an acetate, a carbonate, a oxalate and a halide of such an element. Among compounds of such elements, a titanium compound is preferred. Specifically, the titanium compound may, for example, be a titanium alkoxide such as tetra-n-propyl titanate, tetra-i-propyl titanate, tetra-n-butyl titanate, tetra-n-butyl titanate tetramer, tetra-t-butyl titanate, tetracyclohexyl titanate, tetraphenyl titanate or tetrabenzyl titanate, a titanium oxide obtainable by the hydrolysis of a titanium alkoxide, a titanium/silicon or zirconium double oxide obtainable by the hydrolysis of a mixture of a titanium alkoxide with a silicon alkoxide or a zirconium alkoxide, titanium acetate, titanium oxalate, titanium potassium oxalate, titanium sodium oxalate, potassium titanate, sodium titanate, a titanic acid/aluminum hydroxide mixture, titanium chloride, a titanium chloride/aluminum chloride mixture, 30 titanium bromide, titanium fluoride, potassium hexafluorotitanate, cobalt hexafluorotitanate, manganese hexafluorotitanate, ammonium hexafluorotitanate, or titanium acetylacetone. Among them, a titanium alkoxide such as tetra-n-propyl titanate, tetra-i-propyl titanate or tetra-n-butyl titanate, titanium oxalate or titanium potassium oxalate, is preferred, and tetra-n-butyl titanate is particularly preferred.

35 [0022] Further, with respect to the polycondensation, from the viewpoint of the polycondensability, reduction of by-products such as acetaldehyde, a cyclic trimer, etc. in the obtainable resin and the color tone, as well as the absorbance of the molded product, the temperature-rising crystallization temperature, etc., one polycondensed in the coexistence of (2) a compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, is preferred. Accordingly, the polyester resin of the present invention preferably contains (2) the compound of at least 40 one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) the phosphorus compound.

45 [0023] Here, (2) the compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, may, for example, be an oxide, a hydroxide, an alkoxide, an acetate, a carbonate, an oxalate, a halide, etc. of lithium, sodium, potassium, magnesium, calcium, manganese, iron, cobalt, etc. Specifically, it may, for example, be lithium acetate, sodium acetate, potassium acetate, magnesium oxide, magnesium hydroxide, magnesium alkoxide, magnesium acetate, magnesium carbonate, calcium oxide, calcium hydroxide, calcium acetate, calcium carbonate, manganese oxide, manganese hydroxide, manganese acetate, ferric acetate, cobalt formate, cobalt acetate, cobalt oxalate, cobalt carbonate, cobalt bromide or cobalt acetylacetone. Among them, a magnesium compound or a manganese compound is preferred. 50 Particularly preferred is a magnesium compound, and magnesium acetate is especially preferred.

55 [0024] Further, (3) the phosphorus compound may, specifically, be a pentavalent phosphorus compound, such as orthophosphoric acid, polyphosphoric acid or a phosphoric acid ester such as trimethyl phosphate, triethyl phosphate, tri-n-butyl phosphate, trioctyl phosphate, triphenyl phosphate, tricresyl phosphate, tris(triethylene glycol) phosphate, methyl acid phosphate, ethyl acid phosphate, isopropyl acid phosphate, butyl acid phosphate, monobutyl phosphate, dibutyl phosphate, dioctyl phosphate or triethylene glycol acid phosphate, phosphorous acid, hypophosphorous acid, a phosphorous acid ester such as trimethyl phosphite, diethyl phosphite, triethyl phosphite, trisdodecyl phosphite, trisnonyldecyl phosphite, ethyl diethyl phosphonoacetate or triphenyl phosphite, or a trivalent phosphorus compound such as a metal salt of lithium, sodium, potassium, etc. Among them, a phosphoric acid ester as a pentavalent phos-

phorus compound is preferred. Particularly preferred is trimethyl phosphate or ethyl acid phosphate.

[0025] In the present invention, the respective amounts of (1) the above compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) the above compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) the above phosphorus compound, used at the time of polycondensation, and the respective contents in the resulting polyester resin, are preferably from 0.002 to 1 mol, more preferably from 0.002 to 0.5 mol, as the total amount (T) of atoms of the compound (1), preferably from 0.04 to 5 mol, more preferably from 0.04 to 3 mol, as the total amount (M) of atoms of the compound (2), and preferably from 0.02 to 4 mol, more preferably from 0.02 to 2 mol, as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin.

[0026] When the total amount (T) of atoms of the compound (1), the total amount (M) of atoms of the compound (2) and the total amount (P) of atoms of the compound (3) are within the above ranges, the ultraviolet shielding properties tend to be excellent. Further, particularly, in order to reduce the acetaldehyde content in the molded product and to improve the polycondensability, the total amount (T) of atoms of the compound (1) is more preferably from 0.02 to 0.2 mol, particularly preferably from 0.04 to 0.15 mol, the total amount (M) of atoms of the compound (2) is more preferably from 0.04 to 0.6 mol, particularly preferably from 0.05 to 0.4 mol, most preferably from 0.1 to 0.3 mol, and the total amount (P) of atoms of the compound (3) is more preferably from 0.02 to 0.4 mol, particularly preferably from 0.1 to 0.3 mol, per 1 ton of the polyester resin.

[0027] Further, once the amounts of the respective compounds i.e. (1) the compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) the compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) the phosphorus compound, satisfy the molar amounts of the above ranges as the total amount (T) of atoms of the compound (1), as the total amount (M) of atoms of the compound (2), and as the total amount (P) of atoms of the compound (3), it is preferred that the molar ratio [P/T] of the total amount (P) of atoms of the compound (3) to the total amount (T) of atoms of the compound (1) is from 0.1 to 10, more preferably from 1 to 7, particularly preferably from 2 to 5, and the molar ratio [M/T] of the total amount (M) of atoms of the compound (2) to the total amount (T) of atoms of the compound (1) is from 0.1 to 10, more preferably from 0.5 to 7, particularly preferably from 3 to 5. Further, for a polyester resin particularly excellent in the ultraviolet shielding property, it is preferred that the molar ratio [P/M] of the total amount (P) of atoms of the compound (3) to the total amount (M) of atoms of the compound (2), is more than 0 to 10, more preferably from 1 to 5, particularly preferably from 2 to 4, and the molar ratio [P/(T+M)] of the total amount (P) of atoms of the compound (3) to the sum of the total amount (T) of atoms of the compound (1) and the total amount (M) of atoms of the compound (2), is more than 0 to 10, more preferably from 0.5 to 5, particularly preferably from 1 to 3.

[0028] If the molar ratio [P/T] is less than the above range, the obtainable resin tends to be yellowish, and thus the color tone tends to deteriorate. On the other hand, if it exceeds the above range, the melt polycondensability and the solid phase polycondensability, which will be described hereinafter, tend to deteriorate simultaneously. Further, if the above molar ratio [M/T] is less than the above range, the melt polycondensability and the solid phase polycondensability, which will be described hereinafter, will deteriorate simultaneously, and it tends to be difficult to reduce the acetaldehyde content in the molded product of the resulting resin. On the other hand, if it exceeds the above range, the solid phase polycondensability which will be described hereinafter, tends to deteriorate.

[0029] Further, in the present invention, during the polycondensation, metal compounds other than the above-mentioned respective compounds, may be present within a range not to impair the effects of the present invention, and accordingly, such metal compounds may be contained in the polyester resin of the present invention. In such a case, the metal compounds may, for example, be compounds such as oxides, hydroxides, alkoxides, carbonates, phosphates, carboxylates or halides of aluminum, chromium, nickel, copper, zinc, germanium, molybdenum, silver, tin, lanthanum, cerium, tungsten, gold, etc. The above-mentioned respective compounds and other compounds are preferably ones soluble in water or an alcohol such as ethylene glycol.

[0030] The polyester resin of the present invention is produced by polycondensing a dicarboxylic acid component containing the above terephthalic acid or its ester-forming derivative as the main component and a diol component containing ethylene glycol as the main component in the presence of (1) the compound of at least one element selected from the group consisting of titanium group elements of Group 4A of the periodic table, preferably in the coexistence of (2) the compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) the phosphorus compound, via an esterification reaction or an ester exchange reaction, but basically in accordance with a common process for producing a polyester resin. Namely, it is produced by introducing into a slurry preparation tank the above dicarboxylic acid component containing the above terephthalic acid or its ester-forming derivative as the main component and the diol component containing ethylene glycol as the main component together with optional copolymerizable components, etc., followed by mixing with stirring to obtain a raw material slurry, subjecting it to an esterification reaction for

from about 1 to 10 hours in an esterification reactor under atmospheric pressure or elevated pressure under heating with stirring or to an ester exchange reaction in the presence of an ester exchange catalyst, then transferring the obtained polyester low molecular weight product as the esterification reaction product or the ester exchange reaction product to a polycondensation tank, and melt polycondensing it in the presence of the above-mentioned compounds under atmospheric pressure or gradually reduced pressure under heating with stirring for about 1 to 20 hours. These operations may be carried out by a continuous system or by a batch system.

[0031] At that time, preparation of the raw material slurry comprising the dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component and the diol component containing ethylene glycol as the main component, is carried out preferably by adjusting the molar ratio of the total diol component to the total dicarboxylic acid component to be within a range of from 1.0 to 2.5, more preferably within a range of from 1.03 to 1.7.

[0032] Further, the esterification reaction is carried out by means of a single esterification reactor or a multi-stage reaction apparatus having a plurality of esterification reactors connected in series, under reflux of ethylene glycol, while removing water formed by the reaction and excess ethylene glycol out of the system. At that time, the esterification ratio (the proportion of the esterified by a reaction with the diol component among the total carboxyl groups of the raw material dicarboxylic acid component) of the polyester low molecular weight product as the esterification reaction product or the ester exchange reaction product, is preferably at least 95%. Further, the number average molecular weight of the low molecular weight product is preferably from 500 to 5,000. Further, in the case of the ester exchange reaction, it is necessary to employ an ester exchange catalyst, whereby the transparency of the resulting resin usually tends to be poor. Accordingly, in the present invention, the product is preferably one produced via the esterification reaction.

[0033] With respect to the reaction conditions in the esterification reaction, in the case of a single esterification reactor, the temperature is usually at a level of from 240 to 280°C, the relative pressure to the atmosphere is usually at a level of from 0 to 400 kPa (from 0 to 4 kg/cm<sup>2</sup>G), and the reaction time is from about 1 to 10 hours with stirring. In the case of a plurality of esterification reactors, the reaction temperature in the esterification reactor for the first stage is usually from 240 to 270°C, preferably from 245 to 265°C, and the relative pressure to the atmospheric pressure is usually from 5 to 300 kPa (from 0.05 to 3 kg/cm<sup>2</sup>G), preferably from 10 to 200 kPa (from 0.1 to 2 kg/cm<sup>2</sup>G), and the reaction temperature in the final stage is usually from 250 to 280°C, preferably from 255 to 275°C, and the relative pressure to the atmospheric pressure is usually from 0 to 150 kPa (from 0 to 1.5 kg/cm<sup>2</sup>G), preferably from 0 to 130 kPa (from 0 to 1.3 kg/cm<sup>2</sup>G). Further, the esterification ratio in each stage is preferably adjusted so that its increase will be equal.

[0034] Further, in the esterification reaction, it is possible to suppress production of diethylene glycol as a by-product from ethylene glycol, by adding a small amount of e.g. a tertiary amine such as triethylamine, tri-n-butylamine or benzyl dimethylamine, a quaternary ammonium hydroxide such as tetraethylammonium hydroxide, tetra-n-butylammonium hydroxide or trimethylbenzylammonium hydroxide, or a basic compound such as lithium carbonate, sodium carbonate, potassium carbonate or sodium acetate.

[0035] Further, the melt polycondensation is carried out under reduced pressure, while distilling off formed ethylene glycol out of the system, by means of a single melt polymerization tank, or a multi-stage reaction apparatus having a plurality of melt polycondensation tanks connected in series, for example, an apparatus comprising a perfect mixing type reactor equipped with stirring vanes for the first stage and horizontal plug flow type reactors equipped with stirring vanes for the second and third stages.

[0036] With respect to the reaction conditions in the melt polycondensation, in the case of a single polycondensation tank, the temperature is usually from about 250 to 290°C, the pressure is gradually reduced from the atmospheric pressure, so that finally, the absolute pressure will be usually at a level of from 1.3 to 0.013 kPa (from 10 to 0.1 Torr), and the reaction time is from about 1 to 20 hours with stirring. Whereas, in the case of a plurality of polycondensation tanks, the reaction temperature in the polycondensation tank for the first stage is usually from 250 to 290°C, preferably from 260 to 280°C and the absolute pressure is usually from 65 to 1.3 kPa (from 500 to 10 Torr), preferably from 26 to 2 kPa (from 200 to 15 Torr), and the reaction temperature in the final stage is usually from 265 to 300°C, preferably from 270 to 295°C, and the absolute pressure is usually from 1.3 to 0.013 kPa (from 10 to 0.1 Torr), preferably from 0.65 to 0.065 kPa (from 5 to 0.5 Torr). The reaction conditions for an intermediate stage are selected to be intermediate conditions thereof, and for example, in a three stage reaction apparatus, the reaction temperature in the second stage is usually from 265 to 295°C, preferably from 270 to 285°C, and the absolute pressure is usually from 6.5 to 0.13 kPa (from 50 to 1 Torr), preferably from 4 to 0.26 kPa (from 30 to 2 Torr).

[0037] Further, at the time of polycondensation, timing for addition of (1) the compound of at least one element selected from the group consisting of titanium group elements of Group 4A of the periodic table, (2) the compound of at least one element selected from the group consisting of metal elements of Group 1A of the periodic table, elements of Group 2A of the periodic table, manganese, iron and cobalt, and (3) the phosphorus compound, to the reaction system, may be at any one of an optional stage of a step of preparing a slurry of the starting material terephthalic acid or its ester-forming derivative, ethylene glycol, and optionally employed other dicarboxylic acid components, or a step of the esterification reaction or the ester exchange reaction, or in the initial stage of the melt polycondensation step.

However, the compounds (1) and (2) are added preferably in the step of the esterification reaction or the ester exchange reaction, or in the stage of transportation to the melt polycondensation step, and it is also preferred that they are added at a stage where the esterification ratio of the esterification reaction product or the ester exchange reaction product reaches at least 90%. Further, it is preferred that the compound (1) is added later than the compound (2). Further, it is preferred that the compound (3) is added at a stage where the esterification ratio of the esterification reaction product or the ester exchange reaction product is less than 90%.

5 [0038] With respect to the specific steps for addition of the respective compounds, it is preferred, for example, that the compound (1) is added to the esterification reaction tank for the final stage in the multi-stage reaction apparatus or to the esterification reaction product or the ester exchange reaction product in the stage for transportation to the melt polycondensation step, and the compound (2) is added to the esterification reaction tank for the final stage in the multi-stage reaction apparatus. Further, the compound (3) is preferably added to the slurry preparation tank or the esterification reaction tank for the first stage, particularly preferably to the slurry preparation tank. Namely, in the present invention, it is preferred to set the order of addition of the respective compounds (1), (2) and (3) to the reaction system to be (3) then (2) and then (3).

10 15 [0039] By setting the timing of addition and the order of addition of the respective compounds (1), (2) and (3) to the reaction system as mentioned above, the thermal stability of the resin can be improved, and production of diethylene glycol as a by-product in the reaction system which causes production of acetaldehyde, etc. as by-products during the melt molding, can be suppressed, and further, it is possible to effectively obtain the effects for improving the melt polycondensability and the solid phase polycondensability.

20 25 [0040] Further, addition of the respective compounds (1), (2) and (3) to the reaction system at the time of the polycondensation, is preferably carried out in the form of a solution in e.g. water or an alcohol such as ethylene glycol. In an ethylene glycol solution in a case where a titanium compound is used as the compound (1), it is preferred to adjust the concentration of titanium atoms to be from 0.01 to 0.3 wt% and the water concentration to be from 0.1 to 1 wt%, from the viewpoint of the dispersibility of the titanium compound in the reaction system and the improvement of the melt polycondensability and the solid phase polycondensability thereby obtainable.

30 [0041] Further, the reaction time for the melt polycondensation is usually preferably at most 3.5 hours. If the reaction time exceeds it, it tends to be difficult to reduce the aldehyde content in the resulting resin and the amount of acetaldehyde by-product during the melt molding.

35 [0042] The polyester resin obtainable by the above melt polycondensation is such that the intrinsic viscosity ( $[\eta_1]$ ) is preferably from 0.35 to 0.75 dL/g, more preferably from 0.50 to 0.60 dL/g, as a value measured at 30°C in a solution in a mixed solvent of phenol/tetrachloroethane (weight ratio: 1/1). If the intrinsic viscosity ( $[\eta_1]$ ) is less than the above range, the withdrawing property from the polycondensation tank, which will be described hereinafter, tends to be poor. On the other hand, if it exceeds the above range, it tends to be difficult to reduce the acetaldehyde content in the resulting resin. Further, the melt polycondensation velocity ( $V_1$ ) as a value obtained by dividing the above-mentioned intrinsic viscosity ( $[\eta_1]$ ) of the resulting polyester resin by the above-mentioned reaction time, is preferably at least 0.15 dL/g/hr.

40 [0043] Further, the resin obtained by the melt polycondensation is usually withdrawn in the form of a strand from a discharge outlet provided at the bottom of the polycondensation tank and, while being cooled by water or after being cooled by water, cut by a cutter into particles such as pellets or chips. Further, such particles after the melt polycondensation, are usually heated at a temperature of from about 60 to 180°C in an atmosphere of an inert gas such as nitrogen, carbon dioxide or argon, or in a steam atmosphere, or in a steam-containing inert gas atmosphere, to crystallize the surface of the resin particles and then subjected to solid phase polycondensation by heat treatment at a low temperature of from immediately below the adhesive temperature of the resin to 80°C in an inert gas atmosphere or/and under a reduced pressure of from 1.3 to 0.013 kPa (from 10 to 0.1 Torr), usually for a period of at most 50 hours, while letting the particles flow not to fuse one another. By this solid phase polycondensation, it is possible to further increase the polymerization degree and to reduce by-products such as acetaldehyde, a cyclic trimer, etc.

45 [0044] The polyester resin obtainable by the above solid phase polycondensation is such that the intrinsic viscosity ( $[\eta_2]$ ) is preferably from 0.70 to 0.90 dL/g, more preferably from 0.70 to 0.80 dL/g, as a value measured at 30°C in a solution in a mixed solvent of phenol/tetrachloroethane (weight ratio: 1/1). Further, the solid phase polycondensation velocity ( $V_2$ ) as a value obtained by dividing the difference ( $[\eta_2]-[\eta_1]$ ) between the above intrinsic viscosity ( $[\eta_2]$ ) of the obtainable solid phase polycondensation resin and the intrinsic viscosity ( $[\eta_1]$ ) of the above-mentioned melt polycondensation resin, by the above-mentioned reaction time, is preferably from 0.008 to 0.015 dL/g/hr. Further, the ratio ( $V_2/V_1$ ) of this solid phase polycondensation velocity to the above-mentioned melt polycondensation velocity is preferably within a range of from 0.04 to 0.07, more preferably within a range of from 0.05 to 0.07.

50 55 [0045] Further, for the purpose of improving the thermal stability, reduction of by-products such as acetaldehyde, a cyclic trimer, etc. during the molding, etc., the resin obtained by the above melt polycondensation or the solid phase polycondensation may usually be subjected to water treatment of dipping it in warm water of at least 40°C for at least 10 minutes, or steam treatment of contacting it with steam or a steam-containing gas of at least 60°C for at least 30

minutes, or treatment with an organic solvent, an acidic aqueous solution of e.g. various mineral acids, organic acids or phosphoric acids, or treatment by an alkaline aqueous solution or an organic solvent solution, of a Group 1A metal, a Group 2A metal or an amine.

5 [0046] Further, the polyester resin of the present invention may contain a crystalline thermoplastic resin different from the polyester resin in a content of from 0.0001 to 1,000 ppm, preferably from 0.0005 to 100 ppm, more preferably from 0.001 to 10 ppm, as the case requires, to adjust the temperature-rising crystallization temperature (Tc) of the resin in the above-mentioned molded product after injection molding to the above-mentioned range. As such a crystalline thermoplastic resin, a polyolefin resin or a polyamide resin may be mentioned as a typical example.

10 [0047] The polyolefin resin may, for example, be a homopolymer of an  $\alpha$ -olefin having from about 2 to 8 carbon atoms, such as ethylene, propylene or butene-1, or a copolymer of such an  $\alpha$ -olefin with another  $\alpha$ -olefin having from 2 to 20 carbon atoms such as ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene or 1-decene, or with a vinyl compound such as vinyl acetate, acrylic acid, methacrylic acid, an acrylate, a methacrylate, vinyl chloride or styrene. Specifically, it may, for example, be an ethylene resin such as an ethylene homopolymer such as a low, intermediate or high density polyethylene, an ethylene/propylene copolymer, an ethylene/1-butene copolymer, an ethylene/4-methyl-1-pentene copolymer, an ethylene/1-hexene copolymer, an ethylene/1-octene copolymer, an ethylene/vinyl acetate copolymer, an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer or an ethylene/ethyl acrylate copolymer, a propylene resin such as a propylene homopolymer, a propylene/ethylene copolymer or a propylene/ethylene/1-butene copolymer, and a 1-butene resin such as a 1-butene homopolymer, a 1-butene/ethylene copolymer or a 1-butene/propylene copolymer.

15 [0048] Further, the polyamide resin may, for example, be a polymer of a lactam such as butyrolactam,  $\delta$ -valerolactam,  $\epsilon$ -caprolactam, enantholactam or  $\omega$ -lauryllactam, a polymer of an amino acid such as 6-amino caproic acid, 7-amino heptanoic acid, 8-amino octanoic acid, 9-amino nonanoic acid, 11-amino undecanoic acid or 12-amino dodecanoic acid, a polycondensate of a diamine, such as an aliphatic diamine such as 1,4-butane diamine, 1,5-pentane diamine, 1,5-hexane diamine, 1,6-hexane diamine, 1,9-nonane diamine, 1,11-undeca diamine, 1,12-dodecane diamine or  $\alpha$ ,  $\omega$ -diaminopolypropylene glycol, an alicyclic diamine such as 1,3- or 1,4-bis(aminomethyl)cyclohexane or bis(p-aminocyclohexylmethane), or an aromatic diamine such as m- or p-xylylene diamine, with a dicarboxylic acid, such as an aliphatic dicarboxylic acid such as glutaric acid, adipic acid, suberic acid, sebacic acid or dodecanoic diacid, an alicyclic dicarboxylic acid such as cyclohexane dicarboxylic acid, or an aromatic dicarboxylic acid such as terephthalic acid or isophthalic acid, or a copolymer thereof. Specifically, for example, nylon 4, nylon 6, nylon 7, nylon 8, nylon 9, nylon 11, 30 nylon 12, nylon 66, nylon 69, nylon 610, nylon 611, nylon 612, nylon 6T, nylon 6I, nylon MXD6, nylon 6/66, nylon 6/610, nylon 6/12, nylon 6/6T or nylon 6I/6T may be mentioned.

35 [0049] In the present invention, the above crystalline thermoplastic resin may be incorporated to the polyester resin by a common method such as a method of directly adding and melt mixing or a method of adding and melt mixing as a master batch the above crystalline thermoplastic resin to the above polyester resin so that its content becomes within the above-mentioned range. Otherwise, a method may be employed wherein the above crystalline thermoplastic resin is directly added as a powder at a production stage of the above polyester resin, for example, at any stage of e.g. during the melt polycondensation (the starting materials, slurry, catalyst, etc.), immediately after the melt polycondensation, immediately after the preliminary crystallization, during the solid phase polycondensation or immediately after the solid phase polycondensation, or during a period after the production stage until the molding stage, or a liquid such as water having the powder dispersed therein, is contacted with the polyester resin chips, a gas such as air having the powder included, is contacted with the polyester resin chips, or the polyester resin chips are contacted to a component made of the crystalline thermoplastic resin under a flowing condition, followed by melt kneading. Among the latter methods, a method is preferred in which the crystalline thermoplastic resin is incorporated to air for pneumatic transportation at the time of pneumatic transportation to a preliminary crystallization machine or at the time of pneumatic transportation to a solid polycondensation tank, of chips of the polyester resin after the melt polycondensation, or at the time of pneumatic transportation to a storage tank or at the time of pneumatic transportation to a molding machine, of chips after the solid phase polycondensation.

40 [0050] Further, in the present invention, the polyester resin may contain, for example, an ultraviolet absorber of e.g. a benzophenone type such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone or 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, a benzotriazole type such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-butylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-octylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-amylophenyl)benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole or 2-(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chlorobenzotriazole, a salicylate type such as phenyl salicylate, p-t-butylphenyl salicylate or p-octylphenyl salicylate, or a cyanoacrylate type such as 2-ethylhexyl-2-cyano-3,3'-diphenylacrylate, and an antioxidant, a photostabilizer, an antistatic agent, a lubricant, a blocking preventive agent, an antifogging agent, a nucleating agent, a plasticizer, a colorant, a filler, etc.

45 [0051] The polyester resin of the present invention may, for example, be molded into a preform by injection molding,

followed by stretch blow molding, or molded into a parison by extrusion, followed by blow molding, to obtain a bottle or the like, or it may be formed into a sheet by extrusion, followed by heat forming to obtain a tray, a container or the like, or said sheet may be biaxially stretched to obtain a film or the like, which will be particularly useful in the field of packaging beverage products. Among them, it is particularly suitable for molding the preform obtained by injection molding into a bottle by a biaxially stretching blow molding method, and it is suitable, for example, for a container for e.g. a carbonated beverage, an alcoholic beverage, or a liquid seasoning such as soy sauce, a regular sauce, Japanese sweet rice wine for cooking or dressing, or after heat setting, for a container which is required to have an aroma-retention property and an ultraviolet shielding property and which is required to be free from an influence over the taste, fragrance, etc., of a beverage such as a fruit juice beverage, a vitamin beverage, a flavor tea or mineral water.

[0052] Now, the present invention will be described in further detail with reference to Examples. However, the present invention is by no means restricted by the following Examples.

## EXAMPLE 1

[0053] Slurries of 43 kg (260 mol) of terephthalic acid and 19 kg (312 mol) of ethylene glycol were continuously supplied over a period of 4 hours to an esterification reaction tank having about 60 kg of bis(hydroxyethyl) terephthalate previously charged and maintained at a temperature of 250°C and a pressure of  $1.2 \times 10^5$  Pa, and even after completion of the supply, the esterification reaction was further carried out for one hour. About one half of this esterification reaction product was transferred to a polycondensation tank.

[0054] Then, to the polycondensation tank to which the esterification reaction product was transferred, from its pipe, ethyl acid phosphate, magnesium acetate and tetra-n-butoxy titanium were sequentially added in their ethylene glycol solutions, respectively, with intervals of 5 minutes, so that 0.387 mol of phosphorus atoms (P), 0.062 mol of magnesium atoms (Mg) and 0.063 mol of titanium atoms (Ti) would remain per 1 ton of the resulting polyester resin. Then, the interior of the system was heated from 250°C to 280°C over a period of 2 hours and 30 minutes, and at the same time, the pressure was reduced from normal pressure to  $4 \times 10^2$  Pa over a period of one hour, and while maintaining the same pressure, melt polycondensation was carried out for a period of time until the intrinsic viscosity of the obtained resin became 0.55 dL/g. The polymer was withdrawn in the form of a strand from the discharge outlet provided at the bottom of the polycondensation tank, cooled with water and then cut into chips to obtain about 50 kg of a polyethylene terephthalate resin.

[0055] Then, the obtained polyester resin chips were continuously supplied into an agitation crystallizer maintained at about 160°C so that the retention time would be about 5 minutes, for crystallization, then dried at 160°C for 2 hours in a nitrogen stream of 40 L/min in an inert oven ("IPHH-201 model", manufactured by ESPEC), and heated at 210°C for a period of time until the intrinsic viscosity became 0.74 dL/g, for solid phase polycondensation.

[0056] With respect to the obtained polyester resin chips, the contents of copolymerizable components, the contents of metal atoms of the respective metal compounds, the intrinsic viscosity ( $[\eta]$ ), the color coordinate value b as the color tone and the cyclic trimer content (CT) were measured by the following methods, and the results are shown in Table 1.

Content of copolymerizable component

[0057] With respect to a solution having a resin sample dissolved at a concentration of 3 w% in a mixed solvent of deuterated chloroform/hexafluoroisopropanol (weight ratio: 7/3),  $^1\text{H-NMR}$  was measured by a nuclear magnetic resonance apparatus ("JNM-EX270 model", manufactured by Nippon Denshi K.K.), and the respective peaks were identified, whereupon from the integral value of a peak, the content of the copolymerizable component was calculated.

Contents of metal atoms

[0058] 2.5g of a resin sample was ashed and completely decomposed by hydrogen peroxide in the presence of sulfuric acid in accordance with a usual method and then adjusted by distilled water to a constant volume of 50 mL, and with respect to this sample, quantitative analysis was carried out by means of a plasma emission spectrometer (ICP-AES "JY46P model", manufactured by JOBIN YVON COMPANY), whereupon the molar amount per 1 ton of the polyester resin was calculated.

Intrinsic viscosity ( $[\eta]$ )

[0059] 0.25g of a freeze-pulverized resin sample was dissolved at a concentration (c) of 1.0 g/dL in a mixed solvent of phenol/tetrachloroethane (weight ratio: 1/1), at 110°C for 30 minutes in the case of a melt polycondensate resin, or at 120°C for 30 minutes in the case of a solid phase polycondensate resin, whereupon by means of an Ubbelohde capillary viscometer, the relative viscosity ( $\eta_{\text{rel}}$ ) to the solvent was measured at 30°C. A ratio ( $\eta_{\text{sp/c}}$ ) of the specific

viscosity ( $\eta$  sp) obtained from this relative viscosity ( $\eta$  rel)-1, to the concentration (c), was obtained. In a similar manner, the corresponding ratios ( $\eta$  sp/c) were obtained when the concentration (c) was changed to 0.5 g/dL, 0.2 g/dL and 0.1 g/dL, respectively. From these values, a ratio ( $\eta$  sp/c) when the concentration (c) was extrapolated to be 0, was obtained as the intrinsic viscosity [ $\eta$ ] (dL/g).

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#### Color tone

[0060] A resin sample was filled into a cylindrical powder colorimetric cell having an inner diameter of 36 mm and a depth of 15 mm to be flush, and by means of a colorimetric color difference meter ("ND-300A", manufactured by NIPPON DENSOKU INDUSTRIES CO., LTD.), color coordinate b of the Hunter's color difference formula in the Lab color system as disclosed in Reference 1 of JIS Z8730, was obtained as a simple average value of values measured at four positions by rotating the cell every 90° by a reflection method.

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#### Cyclic trimer content (CT)

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[0061] 4.0 mg of a resin sample was accurately weighed and dissolved in 2 mL of a mixed solvent of chloroform/hexafluoroisopropanol (volume ratio: 3/2), and then further diluted by an addition of 20 mL of chloroform. Then, 10 mL of methanol was added thereto for reprecipitation, followed by filtration to obtain a filtrate, which was evaporated to dryness. Then, the residue was dissolved in 25 mL of dimethylformamide. The amount of a cyclic trimer (cyclotriethylene terephthalate) in this solution was quantitatively analyzed by liquid chromatography ("LC-10A", manufactured by Shimadzu Corporation).

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[0062] Then, the obtained resin was dried at 160°C for at least 16 hours in a vacuum dryer ("DP-41 model", manufactured by YAMATO CHEMICAL INDUSTRY CO., LTD.). Then, by an injection molding machine ("M-70All-IDM", manufactured by Meiki Co., Ltd.), a stepped molded plate having the shape as shown in Fig. 1 and having a size of 50 mm × 100 mm and thicknesses of six steps ranging from 6 mm to 3.5 mm in a transverse direction with each step being 0.5 mm, was injection-molded at a cylinder temperature of 280°C under a back pressure of  $5 \times 10^5$  Pa at an injection rate of 40 cc/sec under a dwell pressure of  $35 \times 10^5$  Pa at a mold temperature of 25°C and with a molding cycle of about 75 seconds. Further, in Fig. 1, G indicates a gate portion.

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[0063] With respect to the molded plate thus obtained, the absorbance at a wavelength of 395 nm and 500 nm, and the temperature-rising crystallization temperature (Tc) were measured by the following methods, and the results are shown in Table 1.

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#### Absorbance

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[0064] The portion having a thickness of 3.5 mm (portion A + B in Fig. 1) in the molded plate, was measured by means of a ultraviolet visible light spectrophotometer ("UV-2400", manufactured by Shimadzu Corporation) at a scanning speed adjusted to be a low speed mode (127 nm/min within a wavelength range of from 300 to 800 nm with a slit width of 5 nm at a sampling pitch of 0.5 nm by a transmission mode, whereby the differences from the absorbance at a wavelength of 800 nm, of the absorbances at wavelengths of 395 nm and 500 nm, were obtained.

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#### Temperature-rising crystallization temperature (Tc)

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[0065] The forward end portion (portion A in Fig. 1) having a thickness of 3.5 mm in the molded plate, was cut out and dried at 40°C for 3 days by a vacuum dryer, whereupon a sample cut out from the non-surface portion was used, and about 10 mg thereof was accurately weighed and sealed in by means of an aluminum oven pan and a pan cover (normal pressure type, "P/N SSC000E030" and "P/N SSC000E032", manufactured by Seiko Densi K.K.). By means of a differential scanning calorimeter ("DSC220C", manufactured by Seiko K.K.), the sample was heated from 20°C to 285°C at a rate of 20°C/min in a nitrogen stream, and the crystallization peak temperature observed during the temperature rise, was measured.

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[0066] Separately, the obtained polyester resin chips were dried at 130°C for 10 hours by a vacuum dryer. Then, by an injection molding machine ("FE-80S", manufactured by Nissei Plastic Industrial Co., Ltd.), a preform of a test tube shape having an outer diameter of 29.0 mm, a height of 165 mm, an average wall thickness of 3.7 mm and a weight of 60g, was injection-molded at a cylinder temperature of 280°C under a back pressure of  $5 \times 10^5$  Pa at an injection rate of 45 cc/sec under a dwell pressure of  $30 \times 10^5$  Pa at a mold temperature of 20°C with a molding cycle of about 40 seconds.

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[0067] Such preforms were heated for 70 seconds in a near infrared ray irradiation furnace equipped with a quartz heater, then left at room temperature for 25 seconds and then introduced into a blow mold set at 160°C and subjected to blow molding under a blow pressure of about  $7 \times 10^5$  Pa for one second and then under a blow pressure of about

30  $\times 10^5$  Pa for 40 seconds for heat setting, while stretching it in the height direction by a stretching rod, followed by cooling in air to obtain 500 bottles having an outer diameter of about 95 mm, a height of about 305 mm, an average wall thickness of the body portion of about 0.37 mm, a weight of about 60g and an internal capacity of about 1.5ℓ. With respect to the obtained 498th to 500th bottles, the aroma-retention property was measured and evaluated by the following method, and the results are shown in Table 1.

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#### Aroma-retention property

[0068] In a bottle, a 100% orange juice was filled in a hot state, tightly sealed with a cap and stored at 10°C for one month, whereupon the cap was removed, and the aroma was subjected to a sensory test by comparing it with a case where the orange juice was stored under the same conditions in a glass bottle, whereby evaluation was made under the following standards.

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O: there was no difference in aroma from the glass bottle, and the aroma-retention property was good.

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Δ: the aroma was weak as compared with the glass bottle, and the aroma-retention property was slightly poor.

×: the aroma was extremely weak as compared with the glass bottle, and the aroma-retention property was inferior.

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[0069] Further, with respect to the obtained 491st to 500th bottles, the surface appearance of the body portion of each bottle was visually observed and evaluated under the following standards, to evaluate the mold contamination, and the results are shown in Table 1.

◎ : the surface was smooth, and no mold contamination was observed.

O: the surface smoothness was slightly inferior, and accordingly, the mold contamination was slightly observed but was not practically problematic.

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×: the surface was roughened, deposition of foreign matters was observed, and the mold contamination was substantial.

#### EXAMPLES 2 to 6

[0070] The operation was carried out in the same manner as in Example 1 except that the amounts of ethyl acid phosphate, magnesium acetate and tetra-n-butoxy titanium at the time of the melt polycondensation were changed as shown in Table 1, and then results are shown in Table 1.

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#### EXAMPLE 7

[0071] The operation was carried out in the same manner as in Example 2 except that the solid phase polycondensation polyester resin obtained in Example 2 was further subjected to water treatment by immersing it in hot water of 90°C for two hours, and the results are shown in Table 1.

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#### EXAMPLE 8

[0072] The operation was carried out in the same manner as in Example 7 except that the polyester resin obtained in Example 7 was used, and a low density polyethylene was added at the time of the injection molding of the stepped molding plate and at the time of the injection molding of the preform, and the results are shown in Table 1.

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#### COMPARATIVE EXAMPLE 1

[0073] The operation was carried out in the same manner as in Example 1 except that at the time of the melt polycondensation, ethyl acid phosphate, magnesium acetate and antimony trioxide were sequentially added in their ethylene glycol solutions, respectively, with intervals of 5 minutes, and the respective amounts were adjusted as shown in Table 1, and the results are shown in Table 1.

#### COMPARATIVE EXAMPLE 2

[0074] The operation was carried out in the same manner as in Example 1 except that at the time of the melt polycondensation, orthophosphoric acid and germanium dioxide were sequentially added in their ethylene glycol solutions, respectively, with intervals of 5 minutes, and the respective amounts were adjusted as shown in Table 1, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 3

[0075] The operation was carried out in the same manner as in Comparative Example 2 except that the amount of germanium dioxide was changed, and the obtained solid phase polycondensation polyester resin was further subjected to water treatment by dipping it in hot water at 90°C for 4 hours, and the results are shown in Table 1.

COMPARATIVE EXAMPLE 4

[0076] The operation was carried out in the same manner as in Example 1 except that at the time of the melt poly-condensation, tetra-n-butoxy titanium, magnesium acetate and ethyl acid phosphate were sequentially added in their ethylene glycol solutions, respectively, with intervals of 5 minutes, and the respective amounts were adjusted as shown in Table 1, and the results are shown in Table 1.

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Table 1

		Examples						
		1	2	3	4	5	6	7
Copolymerizable components	Diethylene glycol (mol% based on diol)	1.8	1.7	1.8	1.6	1.6	1.7	1.7
Contents of metal atoms	Titanium atoms (T) (mol/t)	0.063	0.063	0.063	0.063	0.125	0.063	0.063
	Magnesium atoms (M) (mol/t)	0.062	0.123	0.247	0.123	0.247	0.123	0.123
	Germanium atoms (Ge) (mol/t)							
	Antimony atoms (Sb) (mol/t)							
	Phosphorus atoms (P) (mol/t)	0.387	0.387	0.387	0.194	0.065	0.387	0.387
P/T	(mol/mol)	6.14	6.14	6.14	3.08	1.03	3.10	6.14
M/T	(mol/mol)	0.98	1.95	3.92	1.95	1.98	1.95	1.95
P/M	(mol/mol)	6.24	3.15	1.57	1.58	0.53	1.57	3.15
P/(T+M)	(mol/mol)	3.10	2.08	1.25	1.04	0.35	1.04	2.08
Resin chips	Intrinsic viscosity $[\eta]$ (dL/g)	0.74	0.75	0.75	0.73	0.74	0.75	0.75
	Color coordinate b	+2.6	+1.8	+2.4	+2.4	+3.4	+4.7	+1.8
	Cyclic trimer content (CT) (wt%)	0.29	0.32	0.33	0.29	0.27	0.22	0.32
Stepped molded plate	Absorbance 395 nm	0.16	0.11	0.15	0.14	0.19	0.26	0.11
	500 nm	0.02	0.02	0.02	0.02	0.02	0.02	0.02
	Temperature-rising crystallization temperature (Tc) (°C)	165	166	165	172	178	165	161
Bottle	Aroma-retention property	○	○	○	○	○	○	○
	Mold contamination property	○	○	○	○	○	○	○

Table 1 (continued)

	Copolymerizable components	Diethylene glycol (mol% based on diol)	Comparative Example			
			1	2	3	4
Contents of metal atoms	Titanium atoms (T) Magnesium atoms (Mg) Germanium atoms (Ge) Antimony atoms (Sb) Phosphorus atoms (P)	(mol/t) (mol/t) (mol/t) (mol/t) (mol/t)	3.5 2.057 0.551 1.372 2.906	2.5 0.716 0.716 0.969 0.969	2.5 0.716 0.969 0.969 0.549	1.086 2.180 1.086 2.180 0.549
P/T	(mol/mol)	—	—	—	—	0.5
M/T	(mol/mol)	—	—	—	—	2.00
P/M	(mol/mol)	1.41	—	—	—	0.25
P/(T+M)	(mol/mol)	—	—	—	—	0.17
Resin chips	Intrinsic viscosity [η] (dL/g) Color coordinate b Cyclic trimer content (CT) (wt%)	0.78 +0.8 0.40	0.76 +0.9 0.42	0.76 +1.2 0.32	0.75 +14.3 0.34	
Stepped molded plate	Absorbance 395 nm 500 nm Temperature-rising crystallization temperature (Tc) (°C)	0.04 0.01 142	0.06 0.01 168	0.05 0.01 166	0.42 0.06 153	
Bottle	Aroma-retention property Mold contamination property	X O	△ O	△ O	△ O	X X

## EXAMPLE 9

[0077] Using a continuous polymerization apparatus comprising a slurry preparation tank, esterification reactors of two stages connected in series thereto and melt polycondensation tanks of three stages connected in series to the second stage esterification reactor, terephthalic acid and ethylene glycol were continuously supplied in a weight ratio of 865:485 to the slurry preparation tank, and a 0.3 wt% ethylene glycol solution of ethyl acid phosphate, was continuously added in such an amount that the content as phosphorus atoms (P) per 1 ton of the formed polyester resin would be 0.194 mol, followed by stirring and mixing to obtain a slurry. This slurry was transferred to the first stage esterification reactor set for an average retention time of 4 hours in a nitrogen atmosphere at 260°C under a relative pressure of 50 kPa (0.5 kg/cm<sup>2</sup>G) and then to the second stage esterification reactor set for an average retention time

of 1.5 hours in a nitrogen atmosphere at 260°C under a relative pressure of 5 kPa (0.05 kg/cm<sup>2</sup>G), to carry out the esterification reaction. At that time, the average esterification ratio as measured by the following method, was 85% in the first stage and 95% in the second stage.

5 Average esterification ratio

[0078] With respect to a solution having a sample dissolved at a concentration of 3 wt% in a mixed solvent of deuterated chloroform/hexafluoroisopropanol (weight ratio: 7/3), <sup>1</sup>H-NMR was measured by a nuclear magnetic resonance apparatus ("JNM-EX270 model", manufactured by Nihon Denshi K.K.), and each peak was identified. The amount of terminal carboxyl groups (A mol/ton sample) was calculated from the integral value of the peak, and by the following formula, the esterification ratio (E%) was calculated as a proportion of the esterified among all carboxyl groups of terephthalic acid units.

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$$\text{Esterification ratio (E)} = [1 - A / (1,000,000 / 192.2) \times 2] \times 100$$

[0079] Further, at that time, via an upper pipe provided at the second stage, a 0.6 wt% ethylene glycol solution of magnesium acetate tetrahydrate was continuously added in such an amount that the content as magnesium atoms (Mg) per 1 ton of the formed polyester resin would be 0.247 mol.

[0080] Continuously, at the time of transporting the esterification reaction product obtained as described above to the melt polycondensation tank, tetrabutyl titanate in the form of an ethylene glycol solution having a concentration of titanium atoms of 0.15 wt% and a water concentration of 0.5 wt%, was continuously added to the esterification reaction product in the transportation pipe in such an amount that the content as titanium atoms (Ti) per 1 ton of the formed polyester resin would be 0.063 mol, and the esterification reaction product was continuously transferred to the first stage melt polycondensation tank set at 270°C under an absolute pressure of 2.6 kPa (20 Torr), then to the second stage melt polycondensation tank set at 278°C under an absolute pressure of 0.5 kPa (4 Torr) and then to the third stage melt polycondensation tank set at 280°C under an absolute pressure of 0.3 kPa (2 Torr), to carry out the melt polycondensation for a total of 3.17 hours by adjusting the retention times in the respective polycondensation tanks so that the intrinsic viscosity ([η<sub>1</sub>]) of the obtained polyester resin would be 0.56 dL/g, whereupon the product is withdrawn in the form of a strand from a discharge outlet provided at the bottom of the polycondensation tank, cooled with water and then cut by a cutter to obtain a polyester resin in the form of chips.

[0081] Then, the polyester resin chips obtained as described above were continuously supplied for crystallization to an agitation crystallization machine held at about 160°C in a nitrogen atmosphere so that the retention time would be about 60 minutes and then continuously supplied to a tower type solid polycondensation apparatus and heated at 205°C in a nitrogen atmosphere for 19 hours for solid phase polycondensation by adjusting the retention time so that the intrinsic viscosity ([η<sub>2</sub>]) of the obtained polyester resin would be 0.75 dL/g. The intrinsic viscosity ([η<sub>1</sub>]) of the above melt polycondensate resin and the intrinsic viscosity ([η<sub>2</sub>]) of the solid polycondensate resin, were measured by the above-mentioned method.

[0082] Further, the melt polycondensation rate (V<sub>1</sub>) as a value obtained by dividing the intrinsic viscosity ([η<sub>1</sub>]) of the above melt polycondensate resin by the melt polycondensation time, the solid phase polycondensation rate (V<sub>2</sub>) as a value obtained by dividing the difference ([η<sub>2</sub>] - [η<sub>1</sub>]) between the above intrinsic viscosity ([η<sub>2</sub>]) of the above solid polycondensate resin and the intrinsic viscosity ([η<sub>1</sub>]) of the above melt polycondensate resin, by the solid phase polycondensation time, and the ratio (V<sub>2</sub>/V<sub>1</sub>) of the solid phase polycondensation rate (V<sub>2</sub>) to the melt polycondensation rate (V<sub>1</sub>), were calculated, respectively, and the results are shown in Table 2.

[0083] Further, with respect to the obtained solid phase polycondensate resin chips, the contents of titanium atoms (Ti), magnesium atoms (Mg) and phosphorus atoms (P) of the titanium component, the magnesium component and the phosphorus component, respectively, per 1 ton of the resin, were measured by the above-mentioned methods, and the results are shown in Table 2.

[0084] Further, with respect to the obtained solid phase polycondensate resin chips, the copolymerized amount of diethylene glycol, the cyclic trimer content (CT) and the color coordinate value b as the color tone, were measured by the above-mentioned methods, and the acetaldehyde content (AA<sub>1</sub>) was measured by the following method. The results are shown in Table 2.

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Acetaldehyde content (AA<sub>1</sub>)

[0085] 5.0g of a resin sample was accurately weighed and sealed in together with 10 mL of pure water in a micro

bomb having an internal capacity of 50 mℓ under sealing with nitrogen, whereupon heat extraction was carried out at 160°C for 2 hours. The amount of acetaldehyde in the extracted solution was quantitatively analyzed by gas chromatography ("GC-14A", manufactured by Shimadzu Corporation) using isobutyl alcohol as the internal standard.

5 [0086] Then, the obtained resin was dried at 160°C for 4 hours in a nitrogen stream of 40 ℓ/min in an inert oven ("IPHH-201 model", manufactured by ESPEC COMPANY), and then, by an injection molding machine ("M-70AII-DM", manufactured by Meiki Co., Ltd.), a stepped molded plate having a shape shown in Fig. 1, was injection-molded at a cylinder temperature of 280°C under a back pressure of  $5 \times 10^5$  Pa at an injection rate of 40 cc/sec under a dwell pressure of  $35 \times 10^5$  Pa at a mold temperature of 25°C with a molding cycle of about 75 seconds.

10 [0087] With respect to the molded plate, the absorbances at wavelengths of 395 nm and 500 nm were measured by the above-mentioned method, and further, the acetaldehyde content (AA<sub>2</sub>) and the haze, were measured by the following methods. The results are shown in Table 2.

#### Acetaldehyde content (AA<sub>2</sub>)

15 [0088] Using samples cut out in the form of chips of about 4 × 4 mm from the rear end portion having a thickness of 3.5 mm (portion B in Fig. 1) in the molded plate, the measurement was carried out by the same method as described above.

#### Haze

20 [0089] With respect to the portion having a thickness of 5.0 mm (portion C in Fig. 1) in the molded plate, the haze was measured by means of a haze meter ("NDH-300A", manufactured by NIPPON DENSHOKU INDUSTRIES CO., LTD.).

25 [0090] Separately, the obtained polyester resin chips were dried at 130°C for 10 hours in a vacuum dryer. Then, by an injection molding machine ("FE-80S", manufactured by Nissei Plastic Industrial Co., Ltd.), a preform of a test tube shape having an outer diameter of 29.0 mm, a height of 165 mm, an average wall thickness of 3.7 mm and a weight of about 60g, was injection-molded at a cylinder temperature of 280°C under a back pressure of  $5 \times 10^5$  Pa at an injection rate of 45 cc/sec under a dwell pressure of  $30 \times 10^5$  Pa at a mold temperature of 20°C with a molding cycle of about 40 seconds.

30 [0091] The obtained preform was heated for 70 seconds in a near infrared ray irradiation furnace equipped with a quartz heater and then left to stand at room temperature for 25 seconds. Then, it was introduced into a blow mold set at 130°C and blow-molded under a blow pressure of  $7 \times 10^5$  Pa for one second and further under a blow pressure of  $30 \times 10^5$  Pa for 5 seconds, while stretching in the height direction by an stretching rod, heat-set and cooled in air to mold a bottle having an outer diameter of about 95 mm, a height of about 305 mm, an average wall thickness of the body portion of about 0.35 mm, a weight of about 60g and an internal capacity of about 1.5ℓ.

35 [0092] With respect to the obtained bottle, the aroma-retention property and the mold contamination were measured and evaluated by the above-mentioned methods, and further, the acetaldehyde odor was evaluated by the following method. The results are shown in Table 2.

#### Acetaldehyde odor of the bottle

40 [0093] The bottle was heated in an oven at 50°C for one hour, whereupon the acetaldehyde odor was examined by a sensory test and evaluated by five stages ranging from 5 (acetaldehyde odor very little) to 1 (acetaldehyde odor assails ones nostrils).

#### EXAMPLES 10 to 23, and COMPARATIVE EXAMPLES 5 to 7

45 [0094] Polyester resin chips were prepared in the same manner as in Example 9 except that the copolymerizable component and its amount, the amounts and order for addition of the phosphorus compound, the magnesium compound and the titanium compound, the concentration of titanium atoms and the water concentration in the ethylene glycol solution of the titanium compound, and the melt polycondensation time and the solid phase polycondensation time, were changed as identified in Table 2, and evaluated in the same manner. The results are shown in Table 2. In Comparative Example 5, phosphorous acid instead of ethyl acid phosphate, cobalt acetate tetrahydrate instead of magnesium acetate tetrahydrate and titanium potassium oxalate instead of tetrabutyl titanate, were used and added in the order of titanium potassium oxalate, then cobalt acetate tetrahydrate and then phosphorous acid. In Comparative Example 7, orthophosphoric acid was used instead of ethyl acid phosphate, and the order of addition was tetrabutyl titanate, then magnesium acetate tetrahydrate and then orthophosphoric acid.

Table 2

		Examples							
		9	10	11	12	13	14	15	16
Copolymerizable components	Diethylene glycol (mol% based on diol) Isophthalic acid (mol% based on dicarboxylic acid)	2.2	2.2	2.2	2.2	2.2	2.2	1.7	2.2
Ethylene glycol solution of the titanium compound	Concentration of titanium atoms (wt%) Water concentration (wt%)	0.15 0.5	0.15 0.5	0.15 0.5	0.15 0.5	0.15 0.5	0.15 0.5	0.40 1.5	0.40 0.03
Contents of metal atoms	Titanium atoms (T) (mol/t) Magnesium atoms (M) (mol/t)	0.063 0.247	0.063 0.123	0.063 0.370	0.063 0.247	0.125 0.247	0.063 0.247	0.063 0.247	0.063 0.247
Cobalt atoms (P)	Phosphorus atoms (P) (mol/t)	0.194 3.1 3.9 3.9	0.194 3.1 2.0 5.9	0.194 3.1 3.9 3.9	0.065 6.2 3.9 3.9	0.387 3.1 2.0 3.9	0.387 3.1 3.9 3.9	0.194 0.194 0.194 0.194	0.194 0.194 0.194 0.194
P/T M/T	Melt polycondensation time (hr) Intrinsic viscosity [ $\eta_1$ ] (dL/g) Polycondensation rate (V <sub>1</sub> ) (dL/g/hr)	3.17 0.56 0.177	3.33 0.56 0.168	3.00 0.56 0.187	3.33 0.56 0.168	3.00 0.56 0.187	3.17 0.56 0.177	3.25 0.56 0.172	3.25 0.56 0.172
Solid phase polycondensation time	Intrinsic viscosity [ $\eta_2$ ] (dL/g) Polycondensation rate (V <sub>2</sub> ) (dL/g/hr) V <sub>2</sub> /V <sub>1</sub>	19 0.75 0.057	20 0.75 0.060	22 0.75 0.046	18 0.77 0.063	28 0.77 0.045	18 0.76 0.060	20 0.75 0.060	20 0.75 0.055
Resin chips	Acetaldehyde content (AA <sub>1</sub> ) (ppm) Cyclic trimer content (CT) (wt%) Color coordinate b	3 0.28 +2.2	4 0.28 +2.4	4 0.32 +2.2	3 0.24 +3.4	4 0.24 +2.4	4 0.19 +4.7	3 0.27 +2.2	4 0.28 +2.4
Stepped molded plate	Absorbance 395 nm 500 nm Acetaldehyde content (AA <sub>2</sub> ) (ppm) Haze	0.16 0.02 16 7	0.14 0.02 18 8	0.16 0.02 15 8	0.20 0.02 20 7	0.15 0.02 14 8	0.26 0.02 20 8	0.16 0.02 14 4	0.16 0.02 16 12
Bottle	Aroma-retention property Mold contamination property Acetaldehyde odor	○ ○ 4	○ ○ 4	○ ○ 4	○ ○ 5	○ ○ 4	○ ○ 5	○ ○ 4	○ ○ 4

Table 2 (continued)

		Examples						Comparative Examples		
		18	19	20	21	22	23	5	6	
Copolymerizable components	Diethylene glycol (mol% based on diol) Isophthalic acid (mol% based on dicarboxylic acid)	2.2	2.2	2.2	2.2	2.2	2.2	3.1	2.8	
Ethylene Glycol	Concentration of titanium atoms (wt%)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	
Contents of the titanium compound	Water concentration (wt%)	0.5	0.5	0.5	0.5	0.5	0.5	0.03	0.03	
M/T	Titanium atoms (T) (mol/t)	0.010	0.313	0.063	0.063	0.063	0.125	0.021	1.086	
P/T	Magnesium atoms (Mg) (mol/t)	0.247	0.247	0.740	0.247	0.247	1.550	2.180		
Polycondensation rate	Cobalt atoms (M) (mol/t)	0.387	0.387	0.194	0.194	0.775	0.494	1.070	0.549	
V <sub>2</sub> /V <sub>1</sub>	Phosphorus atoms (P) (mol/mol)	37.1	1.2	3.1	0	12.4	3.9	51.2	0.5	
Resin chips	Melt polycondensation time (hr) Intrinsic viscosity [η <sub>1</sub> ] Polycondensation rate (V <sub>1</sub> ) Solid phase polycondensation time (hr) Intrinsic viscosity [η <sub>2</sub> ] Polycondensation rate (V <sub>2</sub> ) Acetaldehyde content (AA <sub>1</sub> ) Cyclic trimer content (CT) Color coordinate <sup>b</sup>	4.00 0.56 0.140 38 0.76 0.005 0.038 4 0.55 +0.6	2.00 0.56 0.280 12 0.76 0.017 0.060 11 0.17 +11.3	3.67 0.56 0.153 26 0.75 0.007 0.048 4 0.28 +2.4	2.83 0.56 0.204 32 0.75 0.006 0.029 4 0.28 +4.2	4.00 0.56 0.198 15 0.77 0.014 0.071 3 0.21 0.027	3.50 0.56 0.140 42 0.77 0.005 0.036 4 0.45 +2.4	3.50 0.56 0.160 43 0.75 0.004 0.028 3 0.49 -2.3	2.00 0.56 0.160 42 0.75 0.005 0.029 3 0.49 +2.2	0.016 0.016 0.057 12 0.75 0.005 0.029 11 0.34 +14.3
Stepped molded plate	Absorbance 395 nm 500 nm Haze	0.09 0.01 18 7	0.31 0.05 30 12	0.20 0.03 21 9	0.21 0.03 14 8	0.27 0.04 28 12	0.10 0.02 13 7	0.06 0.01 27 8	0.42 0.06 35 70	
Bottle	Aroma-retention property Mold contamination property Acetaldehyde odor	○ ○ 4	○ ○ 1	○ ○ 3	○ ○ 5	○ ○ 2	○ ○ 5	○ ○ 2	○ ○ 3	

INDUSTRIAL APPLICABILITY

[0095] According to the present invention, it is possible to provide a polyester resin, whereby a molded product excellent in a gas barrier property and also excellent in an ultraviolet shielding property, color tone, etc., and which is particularly suitable for molding a bottle for e.g. a beverage required to have an aroma-retention property and further to provide a polyester resin, whereby the acetaldehyde content in a molded product is reduced to eliminate an influence over the taste, aroma, etc. of the content, and a process for its production, whereby the polycondensability is improved.

10 **Claims**

1. A polyester resin produced by polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, via an esterification reaction or an ester exchange reaction, characterized in that the content of copolymerized components other than the terephthalic acid component and the ethylene glycol component, is not more than 4 mol% based on the total dicarboxylic acid component, and in a molded product with a thickness of 3.5 mm injection-molded at 280°C, the difference between the absorbance at a wavelength of 395 nm and the absorbance at a wavelength of 800 nm is at least 0.08, and the difference between the absorbance at a wavelength of 500 nm and the absorbance at a wavelength of 800 nm is at most 0.05.
2. The polyester resin according to Claim 1, wherein the temperature-rising crystallization temperature (Tc) of the resin in the molded product after the injection molding at 280°C, is from 150 to 180°C.
- 25 3. The polyester resin according to Claim 1 or 2, wherein the resin before the injection molding is one having an intrinsic viscosity ( $[\eta]$ ) of from 0.70 to 0.90 dl/g and a color coordinate value b of the Hunter's color difference formula of not more than 4.
4. The polyester resin according to any one of Claims 1 to 3, wherein the content of the compound (1) is from 0.002 to 1 mol as the total amount (T) of atoms of the compound (1) per 1 ton of the polyester resin.
- 30 5. The polyester resin according to Claim 4, which is one polycondensed in the coexistence of (2) a compound of at least one element selected from the group consisting of metal elements of Group 1a of the periodic table, elements of Group 11a of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, wherein the content of the compound (2) is from 0.04 to 5 mols as the total amount (M) of atoms of the compound (2) per 1 ton of the polyester resin, and the content of the compound (3) is from 0.02 to 4 mols as the total amount (P) of atoms of the compound (3) per 1 ton of the polyester resin.
- 35 6. The polyester resin according to Claim 5, wherein the contents of the respective compounds (1), (2) and (3) are from 0.02 to 0.2 mol as the total amount (T) of atoms of the compound (1), from 0.04 to 0.6 mol as the total amount (M) of atoms of the compound (2) and from 0.02 to 0.4 mol as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin, the acetaldehyde content (AA<sub>1</sub>) is not more than 5.0 ppm, the acetaldehyde content (AA<sub>2</sub>) of the resin in a molded product after injection-molded at 280°C is not more than 20 ppm, and the haze of a molded product with a thickness of 5 mm after the injection molding at 280°C is not more than 10%.
- 40 7. The polyester resin according to any one of Claims 1 to 6, wherein the compound (1) is a titanium compound, the compound (2) is a magnesium compound, and the compound (3) is a phosphoric acid ester.
8. The polyester resin according to any one of Claims 1 to 7, wherein, as a dicarboxylic acid component, from 0.1 to 50 3 mol% of isophthalic acid or its ester-forming derivative based on the total dicarboxylic acid component, and as a diol component, from 1 to 3 mol% of diethylene glycol based on the total diol component, are copolymerized, respectively.
9. A process for producing a polyester resin, which comprises polycondensing a dicarboxylic acid component containing terephthalic acid or its ester-forming derivative as the main component, and a diol component containing ethylene glycol as the main component in the presence of (1) a compound of at least one member selected from the group consisting of titanium group elements in Group 4A of the periodic table, (2) a compound of at least one element selected from the group consisting of metal elements of Group 1a of the periodic table, elements of Group

IIa of the periodic table, manganese, iron and cobalt, and (3) a phosphorus compound, via an esterification reaction or an ester exchange reaction, characterized in that the amounts of the respective compounds (1), (2) and (3) are such amounts that their contents will be from 0.02 to 0.2 mol as the total amount (T) of atoms of the compound (1), from 0.04 to 0.6 mol as the total amount (M) of atoms of the compound (2) and from 0.02 to 0.4 mol as the total amount (P) of atoms of the compound (3), per 1 ton of the polyester resin.

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10. The process for producing a polyester resin according to Claim 9, wherein the ratio (P/T) of the total amount (P) of atoms of the compound (3) to the total amount (T) of atoms of the compound (1), is from 0.1 to 10.

11. The process for producing a polyester resin according to Claim 9 or 10, wherein the ratio (M/T) of the total amount (M) of atoms of the compound (2) to the total amount (T) of atoms of the compound (1), is from 0.1 to 10.

12. The process for producing a polyester resin according to any one of Claims 9 to 11, wherein the order for addition of the respective compounds (1), (2) and (3) to the reaction system is (3), then (2) and then (1).

15

13. The process for producing a polyester resin according to any one of Claims 9 to 12, wherein the compound (1) is a titanium compound, the compound (2) is a magnesium compound, and the compound (3) is a phosphoric acid ester.

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14. The process for producing a polyester resin according to Claim 13, wherein the titanium compound is added to the reaction system in the form of an ethylene glycol solution having a titanium atom concentration of from 0.01 to 0.3 wt% and a water concentration of from 0.1 to 1 wt%.

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15. The process for producing a polyester resin according to any one of Claims 9 to 14, wherein from 0.1 to 3 mol% of isophthalic acid or its ester-forming derivative is used based on the total dicarboxylic acid component.

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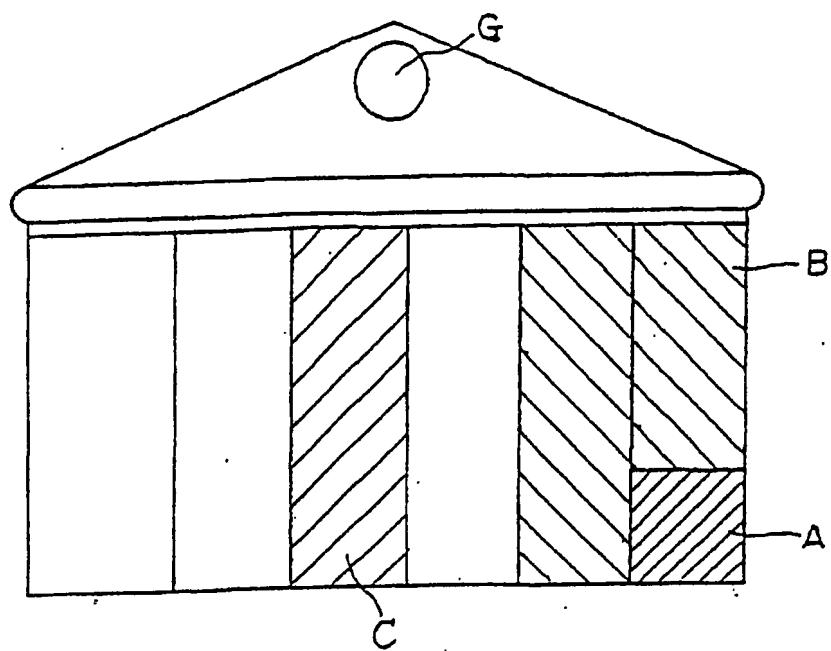
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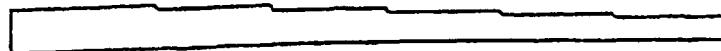
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Fig. 1

(a)



(b)



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/00981

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl<sup>7</sup> C08G63/85

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
Int.Cl<sup>7</sup> C08G63/00-63/91

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-2002 Toroku Jitsuyo Shinan Koho 1994-2002  
Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 53-101093 A (Toyobo Co., Ltd.), 04 September, 1978 (04.09.78), Page 1, lower left column, line 5 to lower right column, line 6 (Family: none)	1-15
P, A	JP 2001-200046 A (Mitsubishi Chemical Corp.), 24 July, 2001 (24.07.01), Column 1, lines 2 to 25 (Family: none)	1-15

 Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
"B"	earlier document but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"Q"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 02 May, 2002 (02.05.02)	Date of mailing of the international search report 21 May, 2002 (21.05.02)
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Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

# IDS REFERENCES



FOR

GB769220

**Title:**  
**Polyglycol terephthalates**

**Abstract:**

In the manufacture of filament-forming phthalate polyglycol terephthalates by heating a glycol ester of terephthalic acid in presence of a metal-containing polymerization catalyst, colour formation is inhibited by effecting polymerization in presence of a phosphoric acid, an alkyl phosphate, a hydroxyalkyl phosphate or an aryl phosphate. The glycol ester is preferably made by heating a dialkyl terephthalate with the glycol in presence of an ester-interchange catalyst. Specified glycols are those of formula OH (CH<sub>2</sub>)<sub>n</sub>OH where n=2-10 and polyethylene glycols of molecular weight 106-6000. Part of the terephthalic acid may be replaced by isophthalic, hexahydroterephthalic, tribenzoic, adipic, azelaic, naphthalic or 2,5-dimethylterephthalic acids or by bis-p-carboxyphenoxyethane. In examples, dimethyl terephthalate and ethylene glycol were heated in presence of a catalyst and after no more methanol was evolved the glycol terephthalate was added to a polymerization vessel, the phosphorus compound added and the whole heated under reduced pressure, the catalyst combination being (1) zinc acetate, tetraisopropyl titanate and tri-(2-hydroxyethyl) phosphate. (2) Magnesium acetate, antimony trioxid and trihexyl phosphate. (3) Zinc acetate, lithium hydride, antimony trioxide and trihexyl phosphate. (4) Lithium hydride, lead monoxide and triphenyl phosphate. (5) Magnesium formate, lead monoxide, antimony trioxide and tributyl phosphate. (6) Lanthanum acetate, antimony trioxide and phosphoric acid or triethyl phosphate. (7) Manganous acetate, antimony trioxide and tricresyl phosphate or phosphoric acid. (8) Calcium acetate monohydrate and phosphoric acid. (9) Manganous acetate, antimony trioxide and tricresyl phosphate. (10) Zinc acetate dihydrate, tetraisopropyl titanate and tri-(2-hydroxyethyl) phosphate. Phosphoric compounds referred to in addition to those exemplified are tri-isopropyl-, triamyl- and tributyl-phosphates; also diphenyl ethyl phosphate, diphenyl phosphate, dibutyl phenyl phosphate, tri-(3-hydroxypropyl) phosphate, dibutyl hydrogen phosphate and phenyl dihydrogen phosphate. Specification 578,079, [Group IV], is referred to.

# PATENT SPECIFICATION

769,220



Date of Application and filing Complete

Specification: Sept. 10, 1954.

No. 26260/54

Application made in United States of America on Sept. 30, 1953.

Application made in United States of America on Sept. 30, 1953.

Complete Specification Published: March 6, 1957.

Index at acceptance:—Class 2(5), R3D(1:2:4:6).

International Classification:—C08g.

## COMPLETE SPECIFICATION

### Polyglycol Terephthalates

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, located at 5 Wilmington 98, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved method for the preparation of polymeric esters and more particularly to the preparation of polymeric glycol terephthalates. 15 A novel class of fiber- and film-forming polymers consisting of polyesters of terephthalic acid and polymethylene glycols containing from 2 to 10 carbon atoms is disclosed in British Patent Specification No. 20 578,079. A commercially important example of this class is polyethylene terephthalate, which is prepared by carrying out an ester interchange reaction between ethylene glycol and dimethyl terephthalate (DMT) followed 20 by polymerization at elevated temperatures and reduced pressures. In effecting these ester interchange and polymerization reactions various catalytic agents have been employed to accelerate the rate of reaction. 25 However, the use of catalytic systems in polymer preparation has also been attended by the development of color in the polymer, the extent of color formation being dependent on the particular nature of the catalyst. A process for retarding the formation of color during polymerization without seriously impairing catalytic activity would be of great importance in preparing polyethylene terephthalate for many commercial uses, and this 30 applies especially to textile uses, for which colorless or white fibers are greatly desired. Even more desirable is a polymerization in which colorless products are produced at rates even faster than heretofore attained. 35 An object of this invention is the provision of a process for producing polymeric esters rapidly. A further object is the pro-

duction in a rapid manner of such esters which are substantially free of color. Other objects appear hereinafter. 50

The invention consists in a process for the production of polyglycol terephthalates which comprises heating a substantially monomeric glycol ester of terephthalic acid in the presence of a metal-containing poly- 55 merization catalyst and a phosphorus compound selected from the group consisting of phosphoric acid, alkyl phosphates, hydroxy-alkylphosphates and aryl phosphates under reduced pressure until a filament-forming 60 polymer is produced.

The invention may be carried out by reacting one or more glycols and terephthalic acid or an ester thereof in an esterification or ester interchange reaction to produce a glycol 65 terephthalate. This ester compound is in substantially monomeric form and is exemplified by the reaction product of ethylene glycol and dimethyl terephthalate, namely, bis-(2-hydroxyethyl) terephthalate. 70

The monomer may be formed by an ester interchange or other esterification reaction. The esterification may be effected in the presence of an esterification catalyst. The esterification and polymerization catalysts 75 may be the same but preferably are different, and, if different, may be added immediately before each respective reaction. If the catalysts are the same, the addition of a single amount of it may occur prior to the first 80 step. In addition to the aforementioned catalysts and in accordance with our invention, the phosphorus compound which modifies the color is added, preferably immediately before the polymerization step, 85 although earlier addition will still effect color modification while perhaps slowing down the esterification reaction.

Polymerization is conducted by heating at elevated temperature under reduced pressure 90 to remove the volatile material produced which is chiefly the glycol used, being ethylene glycol if bis-(2-hydroxyethyl) terephthalate is being polymerized. The modifiers

of this invention operate with the wide variety of catalysts used in the preparation of glycol terephthalate polymers, and by use of the modifiers of this invention substantially colorless polymers are produced at good reaction rates.

The following examples illustrate the principles and practice of this invention and are given for illustrative purposes only. All parts and percentages are by weight unless otherwise specified.

#### EXAMPLE 1

The results of a series of experiments on the preparation of polyethylene terephthalate are recorded in Table I. In each case the reaction was carried out in the following manner: 50 parts of dimethyl terephthalate and 50 parts of ethylene glycol were placed in a flask together with the amount of catalyst indicated in the table (percentages calculated on the basis of anhydrous compounds). The flask was fitted with a condenser and heated at atmospheric pressure, whereupon the mixture began to evolve methanol in the range 160-180°C., the temperature depending on the catalyst and its concentration. Heating was continued at such a rate that continuous gentle ebullition was maintained until no further methanol was evolved, the final pot temperature being

about 220°C. in each case. The liquid was then introduced into a polymerization tube together with the indicated amount of modifier, and the mixture was heated at 275°C. 35 under a vacuum of 0.5 to 1.0 mm. of mercury for the indicated length of time. A continuous stream of nitrogen was introduced through a capillary tube to agitate the mixture. At the end of the polymerization period 40 the color of the molten polymer was compared visually with arbitrary color standards consisting of aqueous solutions of du Pont Pontamine Catechu 3 G dye according to the following system of color ratings: 45

- 0 = water.
- 1 = 0.00025 grams of dye per 100 ml of solution.
- 2 = twice as much dye as 1.
- 3 = three times as much dye as 1. 50
- 4 = four times as much dye as 1.
- 5 = etc.

This system of color standards was designed as a measure of the yellowish to brown range of colors generally encountered in the preparation of polyethylene terephthalate. 55

The intrinsic viscosity of the resulting polymer, a measure of the degree of polymerization, was determined in dilute solutions of the polymer in Fomal, which comprises 58.8 parts by weight of phenol and 41.2 parts by weight of trichlorophenol. 60

Catalyst	Mol % <sup>1</sup>	Modifier	TABLE I.				
			Mol % <sup>1</sup>	Pm.T. <sup>2</sup>	I.V. <sup>3</sup>	Color	
			—	4	0.67	12	65
65 1. Zinc Acetate	.. 0.053	None					
Tetraisopropyl	0.007						
Titanate							
Zinc Acetate	.. 0.053	Tri-(2-hydroxyethyl)					
		Phosphate	0.076	4	0.65	5	
70 2. Tetraisopropyl							70
Titanate ..	0.007						
2. Magnesium Acetate	0.24	None	—	2	0.48	2	
Antimony Trioxide	0.020						
Magnesium Acetate	0.24	Trihexyl phosphate	0.125	2	0.42	1	
75 3. Antimony Trioxide	0.020						75
Zinc Acetate ..	0.031	None	—	6	0.75	8	
Lithium Hydride ..	0.122						
Antimony Trioxide	0.020						
Zinc Acetate ..	0.031	Trihexyl Phosphate	0.061	6	0.72	3	
80 4. Lithium Hydride ..	0.122						80
Antimony Trioxide	0.020						
4. Lithium Hydride ..	0.98	None	—	5	0.35	5	
Lead Monoxide ..	0.017						
Lithium Hydride ..	0.98	Triphenyl Phosphate	0.06	5	0.41	3-4	
85 5. Lead Monoxide ..	0.017						85

1. Based on DMT.

2. Polymerization time in hours.

3. Intrinsic Viscosity.

As shown in Table I in every instance when the phosphorus compound of this invention is used the polymer produced has much better color than a polymer produced under the same conditions but in the absence of modifier.

#### EXAMPLE 2

Table II given below lists the results ob-

tained in a series of autoclave preparations of polyethylene terephthalate. In each case 58 parts of dimethyl terephthalate, 40 parts of ethylene glycol and the indicated amount of catalyst were introduced into a stainless steel batch still equipped with a stirrer and a condenser. When the mixture was heated methanol was evolved, the reaction requir-

ing from 2.5 to 4 hours depending on the catalyst and its concentration. The resulting material was transferred to a stainless steel autoclave equipped with a stainless steel 5 stirrer, and the modifier was added in the indicated amount. The reaction mixture was heated to 275°C. and the autoclave was evacuated gradually through an ice trap and a dry ice trap to an absolute pressure of about 0.5 mm. of mercury. After polymerization at this full vacuum for the indicated period of time, the polymer was withdrawn and the molten polymer was compared with the previously described arbitrary color standards. 10 15

TABLE II.

	Catalyst	Mol % <sup>1</sup>	Modifier	Mol % <sup>1</sup>	Pm.T. <sup>2</sup> 3.	I.V. <sup>3</sup> 0.63	Color
1.	Magnesium Formate	0.052	None	—	5	0.65	4 20
20	Lead Monoxide	0.009					
20	Antimony Trioxide	0.020					
	Magnesium Formate	0.052	Tributyl Phosphate	0.06	5	0.65	4
	Lead Monoxide	0.009					
	Antimony Trioxide	0.020					
25	2. Lanthanum Acetate	0.023	None	—	5	0.67	4 25
	Antimony Trioxide	0.020					
	Lanthanum Acetate	0.034	Phosphoric Acid	0.095	6	0.66	2
	Antimony Trioxide	0.033					
	Lanthanum Acetate	0.034	Triethyl Phosphate	0.032	6	0.64	1
	Antimony Trioxide	0.020					
30	3. Manganese Acetate	0.040	None	—	4	0.64	9 30
	Antimony Trioxide	0.020					
	Manganese Acetate	0.040	Tricresyl Phosphate	0.040	8	0.64	1
	Antimony Trioxide	0.020					
35	Manganese Acetate	0.040	Phosphoric Acid	0.065	8	0.68	2 35
	Antimony Trioxide	0.020					

1. Based on DMT.

2. Polymerization time in hours.

3. Intrinsic Viscosity.

Here again, when a modifier of this invention was used, higher quality polymer was obtained. The results in Tables I and II show that phosphoric acid and its esters are useful in producing white or colorless polyethylene terephthalates. Frequently, 45 when some catalyst systems, such as those containing compounds of antimony, lead or arsenic, are used with other additives a grayish cast to the polymer appears. This grayish color is believed to be caused by 50 the reduction of the metallic ions to the metal. A distinct advantage of the modifiers of this invention lies in the fact that there is no such effect, and the polymers produced are entirely free from the grayish color when 55 the phosphoric acid or esters are used with the above-mentioned catalysts.

## EXAMPLE 3

Ninety parts of ethylene glycol was heated with 28.1 parts of dimethyl terephthalate 60 and about 0.073 part calcium acetate monohydrate until the theoretical quantity of methanol (9.25 parts) had been removed. The resulting mixture was dissolved in water, heated to 80°C., filtered, and cooled to 50°C., 65 whereupon crystals were obtained. The crystals were filtered off and recrystallized from water twice. Of the resulting catalyst-free bis-(2-hydroxyethyl) terephthalate 4.4 parts was placed in a vapor-jacketed glass vessel 70 equipped with a clean stainless steel stirrer. The ester was heated for 6.5 hours at 283°C. under nitrogen at atmospheric pressure with

continuous agitation by the steel stirrer at 100 r.p.m. The resulting liquid had a color of 3 units when compared with the previously 75 described standards. In a second experiment in which 0.14 mol % of phosphoric acid was added to the ester, only 1 unit of color was developed under the same conditions.

Phosphoric acid and its esters also are useful in inhibiting color formation resulting from adventitious catalysis by metallic impurities which might be encountered in commercial practice wherever metallic reaction vessels are used. The surprising ease with 85 which such contamination may occur is illustrated by this example.

In order to obtain the full effect of the modifier, it should be added to the reaction mixture early during the polymerization step, 90 or preferably before polymerization has begun. As shown in the following examples 4 and 5 one function of the inhibitor is to prevent or retard the development of color; when added late in the polymerization step 95 however, the inhibitor appears to have little or no effect on color which has already appeared.

## EXAMPLE 4

Polyethylene terephthalate was prepared 100 in an autoclave following the procedure of Example 2. The catalyst was 0.062 mol % manganese acetate and 0.027 mol % antimony trioxide; no modifier was used. After 3 hours at full vacuum the polymer had developed 7 units of color as compared with

the color standards, and the intrinsic viscosity was 0.67. In another autoclave run the same catalyst system was used, but 0.060 mol % of tricresyl phosphate was added to the reaction mixture after the ester exchange step and before polymerization had begun. The polymer developed 3 units of color after 4.5 hours at full vacuum, and the intrinsic viscosity was 0.65. In a third experiment the mixture was allowed to polymerize under full vacuum for 2 hours without a modifier; 0.060 mol % of tricresyl phosphate was then added and polymerization under full vacuum was continued for 45 minutes. The color of the molten polymer was 8 units, and the intrinsic viscosity was 0.65.

Although the modifiers of this invention must be added to the reaction mixture before polymerization has proceeded to any great extent, it is not necessary that they be present during the ester exchange step to obtain the desired high quality polymer. In fact, it will generally be desirable to omit the modifier during ester exchange when reaction time is a factor, since phosphorus compounds retard the rate of ester exchange. In commercial practice it is desirable to carry out the ester exchange reaction continuously under essentially constant temperature conditions; in such a continuous process the inhibitory effect of phosphorus compounds on the exchange rate is especially serious since a much larger reaction vessel will be required to maintain a given withdrawal rate of product containing a given low percentage of unreacted dimethyl terephthalate.

#### EXAMPLE 5

To a flask equipped with a condenser was added 50 parts of dimethyl terephthalate, 50 parts of ethylene glycol, 0.03 part of zinc acetate dihydrate (0.053 mol % based on DMT), and 0.005 part of tetraisopropyl titanate (0.007 mol % based on DMT). The mixture was heated under atmospheric pressure; at 171°C. methanol began to distil over. Heating was continued at such a rate that continuous gentle ebullition was maintained until no further methanol was evolved, the final pot temperature being about 220°C. The reaction required 1.4 hours. The experiment was repeated with the addition to the reac-

tion mixture of 0.045 part of tri-(2-hydroxyethyl) phosphate (0.076 mol % based on DMT). No methanol was evolved until the temperature of the reaction mixture had reached 180°C., and 1.9 hours were required to complete the evolution of methanol.

#### EXAMPLE 6

The reaction chamber for a constant temperature ester exchange apparatus consisted of a stainless steel beaker, 2 7/8" in diameter and 2 1/4" deep, fitted with a stainless steel cover clamped down with wing nuts and sealed with a gasket prepared from a sheet of polytetrafluoroethylene. The outside of the beaker was electroplated with copper, wound with resistance wire, and insulated. The cover was provided with openings for two thermocouple wells, an inlet tube for a stream of nitrogen gas, and a joint connecting to a column for removal of the methanol. The temperature in the reactor was controlled by a thermocouple acting through a pyrometer controller and the temperature was checked constantly with another thermocouple connected to a potentiometer. The methanol was removed through an electrically heated column equipped with a rotating strip of stainless steel gauze twisted spirally about a vertical shaft; features of this column included good separating efficiency, high throughput rate, and low holdup. The jacket temperature was maintained slightly below the boiling point of methanol (65°C.). After passing through the column, the methanol was condensed and collected.

In each run shown in Table III, a charge of 75 parts of dimethyl terephthalate and about 73 parts of glycol was heated to 175°C., whereupon a preheated slurry of the indicated amount of catalyst in 11 additional parts of glycol was introduced. The temperature of the mixture was maintained at 175° ± 2.5°C. throughout the run, and a continuous stream of nitrogen gas was maintained to aid removal of the methanol. The reaction mixture was stirred slowly by a magnetic stirrer in a stainless steel case. The volume of methanol collected after 30, 60 and 120 minutes was recorded and the percentages based on the theoretical yield of methanol are shown in the table.

TABLE III.

105	Catalyst	Mol % (Based on DMT)	Methanol Recovered (% of theoretical)			105
			30 min.	60 min.	120 min.	
1. Manganous Acetate ..	..	0.062	83	92	97	
Antimony Trioxide ..	..	0.020				
Manganous Acetate ..	..	0.062	53	77	90	110
Antimony Trioxide ..	..	0.020				
Dibutyl Hydrogen Phosphate ..	..	0.059				
2. Manganous Acetate ..	..	0.040	68	85	93	
Manganous Acetate ..	..	0.040	51	69	82	
Triethyl Phosphate ..	..	0.086				
Manganous Acetate ..	..	0.040				115
Phosphoric Acid ..	..	0.079				
			No reaction in 75 minutes			

As indicated in the above table there is more unreacted material left after a given time when the modifier is present in the interchange reaction than when it is omitted. Thus, contrary to expectations, a decided advantage is gained when the modifier is added after interchange. The more rapid production of polymer, that is, amount of polymer per unit of time, is an outstanding 10 feature of this invention.

As can be seen from the above examples, the modifiers of this invention are added to a monomeric glycol terephthalate which has an intrinsic viscosity of substantially zero 15 (say 0.0 to 0.15) and the heating of the modified reaction media is continued until the intrinsic viscosity of the resultant polymer is about 0.5 or higher. Vacuum is applied to remove volatile material and to bring polymerization to the desired level.

Among the modifiers that may be used are the triaryl phosphates, such as triphenyl phosphate, and the trialkyl phosphates, such as triethyl phosphate, tri-isopropyl phosphate, triamyl phosphate, tributyl phosphate and trihexyl phosphate. Still others include 25 diphenyl ethyl phosphate, diphenyl phosphate and dibutyl phenyl phosphate. Glycol esters of phosphoric acid, such as tri-(2-30 hydroxyethyl) phosphate and tri(3-hydroxypropyl) phosphate are especially useful additives. Partially esterified phosphoric acids, such as dibutyl hydrogen phosphate and phenyl dihydrogen phosphate also are very 35 useful. Phosphoric acid itself may be added in the form of orthophosphoric acid, pyrophosphoric acid, metaphosphoric acid or in other forms differing in degree of hydration. One advantage of the modifiers of this 40 invention lies in their chemical simplicity. Complicated structures are not involved. In fact it is preferred to use modifiers which do not contain nitrogen or halogen atoms such as chlorine. The modifiers of this invention 45 are inexpensive and readily available.

Further, they are very effective and only small amounts need be used. The amount of the phosphoric acid or phosphate ester added will depend in part on the amount of 50 catalyst used. Usually it will be desirable to use an amount in the range of about 0.05 to about 2.0 mols of modifier for each mol of catalyst, based on the total number of mols of all catalysts if more than one catalyst is used. If less than 0.05 mol is used, the effect is very small. On the other hand, the addition in excess of 2 mols will produce little additional advantage.

The phosphate modifiers employed in this 60 invention can be used with any of the well-known catalysts or catalyst combinations effective in the preparation of the polyesters. In practical applications a system of two or more catalysts will generally be used containing one or more components especially

effective in promoting the ester exchange reaction between ethylene glycol and dimethyl terephthalate together with one or more additional components which are effective in promoting the polymerization of the monomeric glycol terephthalate. Examples of catalytic materials useful in the ester exchange reaction include the alkali metals and their hydrides and compounds of certain metals, such as calcium, magnesium, lanthanum, manganese, and cobalt. Many of these catalysts also are effective in the initial stages of polymerization, but it will usually be desirable to add a specific polymerization catalyst such as antimony trioxide. Esters 75 of titanium can also be used to catalyze the polymerization reaction. Usually the polymerization catalyst will not retard the rate of ester exchange, and where this is the case it is generally convenient to add all of the 80 catalysts at the beginning of the reaction.

Associated with each catalyst system is a secondary catalytic effect on the reactions of color-forming bodies in the reaction mixture. It is the function of the phosphate additives 90 of this invention to inhibit this secondary catalytic effect without seriously retarding the ability of the catalysts to function in the polymerization reaction. When the tendency of a given catalyst to produce color is high, 95 the phosphate modifiers of this invention will usually operate to reduce the color to acceptable levels. When a catalyst having an inherently low color-forming effect is used, a still further reduction in polymer color is 100 achieved.

Phosphoric acid and the various phosphate esters are substantially equivalent on a molar basis with regard to the inhibition of color. Mixtures of two or more of the phosphate 105 inhibitors are effective to an extent roughly proportional to the total molar quantities used. In using the more volatile members of the group it will frequently be desirable to delay the application of vacuum to the reaction system to allow ester interchange with the glycol to take place. In processes in which the excess glycol is to be recovered and reused, it may be desirable to avoid the use of aryl esters of phosphoric acid. Phenols 110 evolved from these compounds are carried over into the glycol recovery system and are very difficult to remove from the glycol by distillation or other common industrial purification methods. Accumulated phenols 115 would have a deleterious effect on the ester exchange reaction rate.

In commercial applications, it is desirable to combine the recovered glycol with fresh ethylene glycol as new starting material for 125 the reaction; however, ethylene glycol containing phenols as impurities is unsatisfactory because phenols have a deleterious effect on the ester exchange reaction rate. After several cycles, the accumulated phenols build 130

up to intolerably high levels.

Although the process and advantages of the present invention have been particularly described with respect to the preparation of polyethylene terephthalate from dimethyl terephthalate, it should be understood that the invention is fully applicable to the polymerization of bis-(2-hydroxyethyl) terephthalate derived from whatever source and includes the preparation of modified polyethylene terephthalates, i.e., modified with small quantities, e.g., up to 20 mol % based on the terephthalate content of the polyester of other dicarboxylic acids. For example, glycol, terephthalic acid, or a dialkyl ester thereof, and a second acid or ester thereof, may be reacted together to form a copolyester, the second acid being selected from the group consisting of isophthalic acid, bibenzoic acid, hexahydro terephthalic acid, adipic acid, sebatic acid, azelaic acid, the naphthalic acids, 2,5-dimethyl terephthalic acid, and bis-p-carboxyphenoxyethane.

It is also within the scope of the present invention to prepare polyesters by reacting other glycols besides ethylene glycol, such glycols being selected from the series  $\text{HO}(\text{CH}_2)_n\text{OH}$  where "n" is an integer from 2 to 10 inclusive. Polyethylene glycols having molecular weights of about 106 to about 6,000 may also be used in polymer preparation. And, in place of dimethyl terephthalate, there may be employed as monomer any of the terephthalic esters of saturated aliphatic monohydric alcohols containing up to and including 7 carbon atoms.

The products produced by the novel process of this invention are highly desirable. They are color-free polymers which may be readily shaped into films and fibers by conventional spinning techniques, such as by melt spinning. The conditions of polymer preparation and shaping are described in the prior art. For example, such techniques are disclosed in British Patent Specification No. 578,079 and U.S. Patent Nos. 2,534,028, 2,641,592 and 2,647,885 among others.

What we claim is:

1. A process for the production of polyglycol terephthalates which comprises heating a substantially monomeric glycol ester of terephthalic acid in the presence of a metal-

containing polymerization catalyst and a phosphorus compound selected from the group consisting of phosphoric acid, alkyl phosphates, hydroxylalkylphosphates and aryl phosphates under reduced pressure until a filament-forming polymer is produced.

2. The process as claimed in Claim 1 wherein the monomer is formed by reacting one or more glycols with terephthalic acid or an ester or other ester forming derivative thereof.

3. The process as claimed in Claim 2 wherein the monomer forming reaction takes place in the presence of an esterification catalyst.

4. A process as claimed in any of the preceding claims wherein there is present in the reaction mixture a small quantity up to 20 mol % based on the terephthalate content of the polyester of other carboxylic acids or esters thereof selected from the group consisting of isophthalic acid, hexahydroterephthalic acid, bibenzoic acid, adipic acid, sebatic acid, azelaic acid, the naphthalic acids, 2,5-dimethyl terephthalic acid and bis-p-carboxyphenoxyethane.

5. A process in accordance with any of the preceding claims wherein said monomeric glycol ester is bis-(2-hydroxyethyl) terephthalate.

6. A process in accordance with any of the preceding claims in which the amount of the phosphorus compound is from about 0.05 to 85 about 2.0 mols per mol of polymerization catalyst present.

7. A process in accordance with Claim 6 in which the said monomeric ester has an intrinsic viscosity of substantially zero. 90

8. A process in accordance with Claim 6 in which the said heating is continued until the said polymer has an intrinsic viscosity of at least about 0.5.

9. A process in accordance with any of the preceding Claims 2 to 8 in which the terephthalic acid ester employed in the esterification reaction is dimethyl terephthalate.

10. A process in accordance with Claim 9 in which said glycol is ethylene glycol. 100

11. A process for the production of polyglycol terephthalates substantially as hereinbefore described.

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**Title:**

**PRODUCTION OF PARTICULAR POLYESTERS USING A NOVEL CATALYST SYSTEM**

**Abstract:**

This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.6 dL/g comprising reacting the diacid component with the diol component such that a combination of a titanium-based catalyst and a phosphorus-based catalyst is used during the polycondensation steps.

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(54) Title: PRODUCTION OF PARTICULAR POLYESTERS USING A NOVEL CATALYST SYSTEM

(57) Abstract

This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.6 dL/g comprising reacting the diacid component with the diol component such that a combination of a titanium-based catalyst and a phosphorus-based catalyst is used during the polycondensation steps.

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**PRODUCTION OF PARTICULAR POLYESTERS  
USING A NOVEL CATALYST SYSTEM**

**Field of the Invention**

5        This invention relates to a process for preparing modified or unmodified poly(ethylene terephthalate) using a titanium/phosphorus-based catalyst system.

**Background of the Invention**

10      Poly(ethylene terephthalate) may be derived from a process well known in the art comprising direct esterification of ethylene glycol and terephthalic acid. It may also be derived from a process comprising carrying out an ester interchange between ethylene glycol and dimethyl terephthalate to form bis-2-hydroxy ethyl terephthalate which is polycondensed to poly(ethylene terephthalate) under reduced pressure and at elevated temperatures.

15      Problems have also been encountered in the manufacture of poly(ethylene terephthalate) by the ester interchange reaction and by direct esterification reaction. However, this material is slow with respect to ester interchange and is many times impractical with respect to commercial operations. Therefore, it is typical to employ the use of a catalyst during these reactions.

20      Typical catalyst or catalyst systems for polyester condensation are well-known in the art. For example, catalysts disclosed in U.S. Patent Nos. 4,025,492; 4,136,089; 4,176,224; 4,238,593; and 4,208,527, incorporated herein by reference, are deemed suitable in this regard. Further, R. E. Wilfong, Journal of Polymer Science, 54 385 (1961) sets forth typical catalysts which are useful in polyester condensation reactions.

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However, many of these catalysts do not produce finished polyester which has the desired clarity or color.

United States Patent 3,794,592 discloses a method 5 of making polyesters suitable for use in making polyurethanes. More particularly, it discloses a method of making polyesters which have a reduced or controlled rate of reaction with isocyanates. Titanium may be used as a possible catalyst in the esterification and 10 transesterification reactions. Phosphoric acid may be added after the esterification or condensation reaction has been completed. The molecular weight of these products are from about 500 to 10,000 and would not be useful in molding applications.

United States Patent 3,907,754 discloses a catalyst 15 system for the production of poly(ethylene terephthalate) which comprises, in combination, salts of manganese and cobalt with acetyl triisopropyl titanate and a phosphate ester.

United States Patent 4,260,735 discloses the use of 20 an alkanolamine titanium chelate catalyst to esterify and polycondense aromatic polycarboxylic acids or anhydrides, such as terephthalic acid, with a glycol, such as ethylene glycol, at low glycol to acid reactant 25 ratios. The objective of this invention is to make possible commercial production of polyesters with low ether contents, without the addition of any inhibitor to suppress formation of DEG.

United States Patent 4,150,215 discloses a process 30 for preparing high molecular weight polyester resins by reacting ethylene glycol with terephthalic acid in the absence of a catalyst and polymerizing the product under solid state polymerization condition.

United States Patent 3,962,189 discloses a 35 catalyst-inhibitor system for the polymerization of

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poly(ethylene terephthalate) comprising a combination of organic or inorganic salts of manganese and cobalt, titanium alkoxides, organic salts of alkali metals, or alkaline earth metals, and a phosphate ester.

5 United States Patent 4,356,299 discloses a poly(ethylene terephthalate) polycondensation catalyst system comprising a catalyst metal in the form of an alkyl titanate and an antimony compound.

10 Previously, the catalyst systems useful for making poly(ethylene terephthalate) of the prior art employed titanium-based catalysts, phosphorus-based compounds, usually in combination with manganese and/or antimony.

15 Therefore, there has been a need in the art to have a catalyst system which speeds up the reaction so that it is useful for economical purposes and for making a range of molecular weights useful for molding purposes but which also results in a condensation polymer having good clarity and color. Furthermore, environmental concerns demand that the level of catalyst metals be 20 decreased or minimized which is achieved by using the process of this invention.

25 Heretofore, a catalyst system containing low amounts of one or more alkyl titanates in combination with a phosphorus-based compound in order to make poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of sufficient molecular weight to be useful in molding applications has been unknown.

#### Summary of the Invention

30 This invention involves the use of a catalyst system which has the advantages of the prior art with respect to the catalyst system which promotes esterification or transesterification and polycondensation and molecular weight buildup while 35 maintaining good color and clarity.

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This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising:

5           reacting a diacid component further comprising at least 65 mole % terephthalic acid or a diester component comprising at least 65 mole % C<sub>1</sub> - C<sub>4</sub> dialkyl terephthalate and a diol component comprising at least 65 mole % ethylene glycol at

10          temperatures to effect steps (A) and (B) as follows:

(A)        esterification or transesterification, wherein said esterification is carried out, optionally, in the presence of about 1 to about 50, preferably 1 to 20, more preferably 1 to 10 parts of titanium present in the form of an alkyl titanate or

15          optionally, in the presence of a catalyst system comprising from about 1 to about 50, preferably 1 to 20, more preferably 1 to 10 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100, preferably 1 to 50, more preferably 1 to 30, even more preferably 1 to 15 parts of phosphorus in the form of a phosphate ester or phosphoric acid, and

20          wherein said transesterification is carried out in the presence of from about 1 to about 50 parts of titanium in the form of an alkyl titanate; and

25          

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- 5 -

(B) polycondensation, wherein said polycondensation is carried out in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid;

5 each of the parts of the catalyst representing per million parts of polymer product, wherein the mole percentage for all of the diacid component totals 100 mole %, and wherein the mole percentage for all of the diol component totals 100 mole %.

10 In another embodiment of the invention, the process

15 incorporates the use of either an inorganic toner system comprising salts of cobalt and/or an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-aryl amino-1-cyano-3H-dibenz[f,ij]isoquinoline-2,7-dione or at least one

20 copolymerizable blue 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one red anthraquinone or anthrapyridone (6-aryl amino-3H-dibenz[f,ij]isquinoline-2,7-dione) compound at a temperature to effect esterification or ester

25 interchange and polycondensation in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, each of

30 the parts of one catalyst system being per million parts at polymer product and the diacid or diester component totaling 100 mole % and the diol component totaling 100 mole %.

35 Some of the advantages of this invention over the prior art are that: (1) it employs the use of a catalyst

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system containing low amounts of one or more alkyl titanates in combination with a phosphorus-based compound in order to make poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of sufficient 5 molecular weight to be useful in molding applications, (2) the product has good clarity (less haze) and color, (3) there is a lower amount of metal and acetaldehyde in the final product and (4) obtaining a slow crystallization rate in poly(ethylene terephthalate) or 10 modified poly(ethylene terephthalate).

Detailed Description of the Preferred Embodiments

This invention involves a process of producing a moldable polyethylene terephthalate or modified 15 polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g, preferably greater than 0.70 dL/g, comprising reacting a diacid or diester component comprising at least 65 mole % terephthalic acid or C<sub>1</sub> - C<sub>4</sub> dialkylterephthalate, preferably at least 70 mole %, more preferably at least 75 mole %, even more 20 preferably, at least 95 mole %, and a diol component comprising at least 65 mole % ethylene glycol, preferably at least 70 mole %, more preferably at least 75 mole %, even more preferably at least 95 mole %. It 25 is also preferable that the diacid component is terephthalic acid and the diol component is ethylene glycol. The mole percentage for all of the diacid component totals 100 mole %, and the mole percentage for all of the diol component totals 100 mole %.

30 After melt and/or solid phase polycondensation the polyesters have an inherent viscosity (I.V.) of about 0.65 to about 1.2 dL/g, preferably 0.75 dL/g measured at 25°C in a 60/40 ratio by weight of phenol/tetrachloroethane.

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Where the polyester components are modified by one or more diol components other than ethylene glycol, suitable diol components of the described polyesters may be selected from 1,4-cyclohexanedimethanol, 1,2-5 propanediol, 1,3-propanediol, 1,4-butanediol, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-10 cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 2,8-bis(hydroxymethyl)-tricyclo-[5.2.1.0]-decane wherein 2 represents 3, 4, or 5; and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol and the like. In general, these diols contain 2 to 18, preferably 2 to 8 carbon atoms. Cycloaliphatic 15 diols can be employed in their cis or trans configuration or as mixtures of both forms. A preferred modifying diol component is 1,4-cyclohexanedimethanol.

Where the polyester components is modified by one or more acid components other than terephthalic acid, 20 the suitable acid components (aliphatic, alicyclic, or aromatic dicarboxylic acids) of the linear polyester may be selected, for example, from isophthalic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-25 cyclohexanedicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalenedicarboxylic acid and the like. In the polymer preparation, it is often preferable to use a functional acid derivative thereof such as the dimethyl, diethyl, or dipropyl ester of the dicarboxylic acid. 30 The anhydrides or acid halides of these acids also may be employed where practical.

The linear polyesters may be prepared according to 35 polyester forming conditions well known in the art. The reaction should occur at a temperature to effect esterification and polycondensation. For example, a

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mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, or ester forming derivatives thereof, and one or more diols may be heated in the presence of esterification and/or

5        transesterification catalysts at temperatures in the range of about 150° to about 300°C, preferably, about 200°C to about 300°C, and even more preferably, about 260°C to about 300°C, and pressures of atmospheric to about 0.2 mm Hg. Normally, the dicarboxylic acid is  
10      esterified with the diol(s) at elevated pressure and at a temperature at about 240°C to about 270°C. Polycondensation then is effected by increasing the temperature and lowering the pressure while excess diol is removed from the mixture.

15      The reaction is carried out at a temperature to effect esterification or ester interchange and polycondensation in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium in the form of an alkyl titanate and from about 1 to about 20      100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, each of the parts of the catalyst system representing per million parts of polymer product and the diacid or diester component totaling 100 mole % and the diol component totaling 100 mole %.

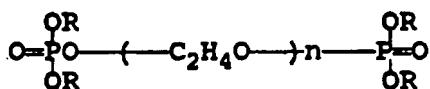
25      Alkyl titanates useful within the context of this invention include: acetyl triisopropyl titanate, titanium tetraisopropoxide, titanium glycolates, titanium butoxide, hexyleneglycol titanate, tetraisoctyl titanate, titanium tetramethylate, 30      titanium tetrabutylate, titanium tetra-isopropylate, titanium tetrapropylate, tetrabutyl titanate, and the like. A preferred alkyl titanate is acetyl triisopropyl titanate.

35      The preferred phosphorus-based compound is a phosphate ester.

- 9 -

It is more preferred that the phosphate ester has the formula

5  
10



15 wherein n has an average value of 1.5 to about 3.0 with about 1.8 being most preferred and each R is hydrogen or an alkyl radical having from 6 to 10 carbon atoms with octyl being most preferred, the ratio of the number of R groups or hydrogen atoms to the number of phosphorus atoms being about 0.25 to 0.50 with about 0.35 being most preferred; and the ester having a free acidity equivalent of about 0.2 to 0.5.

20 25 Other phosphate esters useful in this invention include ethyl acid phosphate, diethyl acid phosphate, triethyl acid phosphate, arylalkyl phosphates, tris-2-ethylhexyl phosphate and the like.

Another preferred phosphorus-based compound is phosphoric acid.

30 It is preferred that the catalyst system of the invention comprises about 3 to about 10 parts of catalyst metal in the form of tetraisopropyl titanate and from about 5 to about 15 parts of phosphorus in the form of said phosphorus-based compound.

35 It is preferred in the process of this invention that the catalyst system further comprises an inorganic toner or an organic toner. Where the toner is an inorganic one, salts of cobalt are preferred. The cobalt toner is usually added after the esterification step before polycondensation when a diacid is reacted. 40 In the case of the reaction at a diester, the toner may

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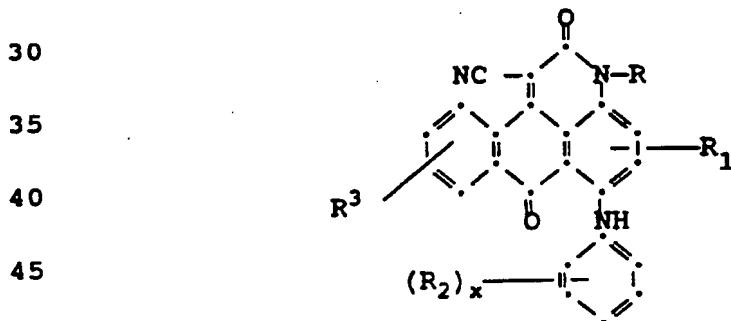
be present during transesterification and during the polycondensation step.

Examples of suitable cobalt salts are cobaltous acetate trihydrate, cobaltous nitrate, cobaltous chloride, cobalt acetylacetanoate, cobalt naphthenate, and cobalt salicyl salicylate and cobalt acetate. It is preferred that the salt of cobalt is cobalt acetate.

When the cobalt salt is cobalt acetate, it is preferable that the cobalt acetate is present in the amount of 10-120 ppm Co, the acetyl triisopropyl titanate is present in the amount of 1-50 ppm Ti, and the phosphorus-based compound is present in the amount of 1-100 ppm phosphorus, all parts by weight based on the total weight of the polymer.

Where the toner is an organic one, it is preferred that the toner is an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-aryl amino-1-cyano-3H-dibenz[f,ij]isoquinoline-2,7-dione or at least one copolymerizable 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one bis anthraquinone or bis anthrapyridone(6-aryl amino-3H-dibenz[f,ij]isquinoline-2,7-dione) compound, wherein the organic toners contain at least one, preferably two polyester reactive groups.

A preferred organic toner comprises at least one 6-aryl amino-1-cyano-3H-dibenz[f,ij]isoquinoline-2,7-diones having the formulae



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wherein

R is hydrogen, cycloalkyl, allyl, alkyl, aryl, aralkyl, alkoxyalkyl or cycloalkylalkylene;

5 R<sub>1</sub> is hydrogen, halogen, alkyl, alkoxy, aryloxy, alkylthio or arylthio;

R<sub>2</sub> is hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, carbalkoxy, carbaryloxy, carbaralkoxy, carboxy, sulfamoyl, alkylsulfamoyl, dialkylsulfamoyl, alkylarylsulfamoyl, cycloalkylsulfamoyl, arylsulfamoyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, alkylarylcarbamoyl, cycloalkylcarbamoyl, arylcarbamoyl, 2-

15 pyrrolidono, acylamido, or N-alkylacylamido;

R<sub>3</sub> is one or more residues selected from the group consisting of hydrogen, halogen, alkyl and alkoxy; and

x is an integer of 1 to 5; wherein one or more of the alkyl, alkoxy, alkoxy, aryl, aryloxy, alkylthio, arylthio or aralkyl residues may contain one or more reactive groups selected from the group consisting of carboxy, carbalkoxy, carbaryloxy, N-alkyl-carbamoyloxy, carbamoyloxy, acyloxy, chlorocarbonyl, hydroxyl, cycloalkylcarbonyloxy, N-

25 arylcarbamoyloxy and N,N-dialkylcarbamoyloxy and wherein said alkyl and aryl groups may contain substituents selected from the group consisting of alkoxy, acyloxy, cyano, hydroxy, halogen and acylamido; wherein at least one polyester reactive group is present to permit copolymerization. These toners are disclosed in United States Patent 4,754,174, which is

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incorporated herein by reference in its entirety.

Even more preferably, the organic compound useful in this invention when copolymerized is

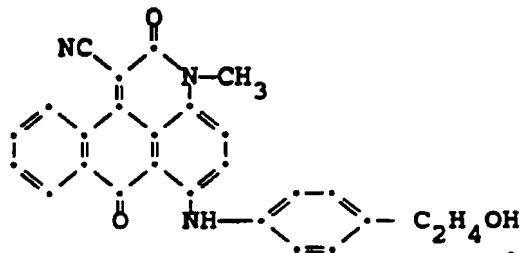
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The preferred organic toner system of this invention are certain blue substituted 1,4-bis(2,6-dialkylanilino) anthraquinones in combination with selected red anthraquinone and anthrapyridone (3H-dibenz[fi,j]isoquinoline-2,7-dione) compounds as disclosed in United States Patent 5,372,864 which is hereby incorporated by reference in its entirety.

35

More particularly, this organic toner system is comprised of at least one blue 1,4-bis(2,6-dialkylanilino) anthraquinone(s) of formula (I):

40

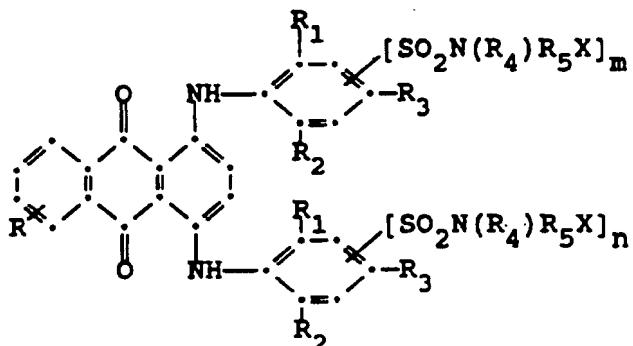
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(I)

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wherein:

R is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl, halogen, carboxy, and C<sub>1</sub>-C<sub>6</sub>

5 alkoxy-C-;

10

$R_1$  and  $R_2$  are independently  $C_1-C_6$ -alkyl;

15  $R_3$  is selected from the group consisting of hydrogen, halogen,  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$  alkyl, hydroxy,  $C_1-C_6$ -alkoxy, substituted  $C_1-C_6$ -alkoxy, cyano, thiocyano,  $C_1-C_6$ -alkylthio, substituted  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylsulfonyl, substituted  $C_1-C_6$ -alkylsulfonyl,  $C_1-C_6$ -alkoxycarbonyl, carboxy, aryloxy, arylthio, arylsulfonyl, and  $SO_2N(R_4)R_5X$  when  $m$  and/or  $n$  are zero;

20

$R_4$  is selected from the group consisting of hydrogen,  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$ -alkyl,  $C_3-C_8$ -alkenyl,  $C_3-C_8$ -alkynyl,  $C_3-C_7$ -cycloalkyl and aryl;

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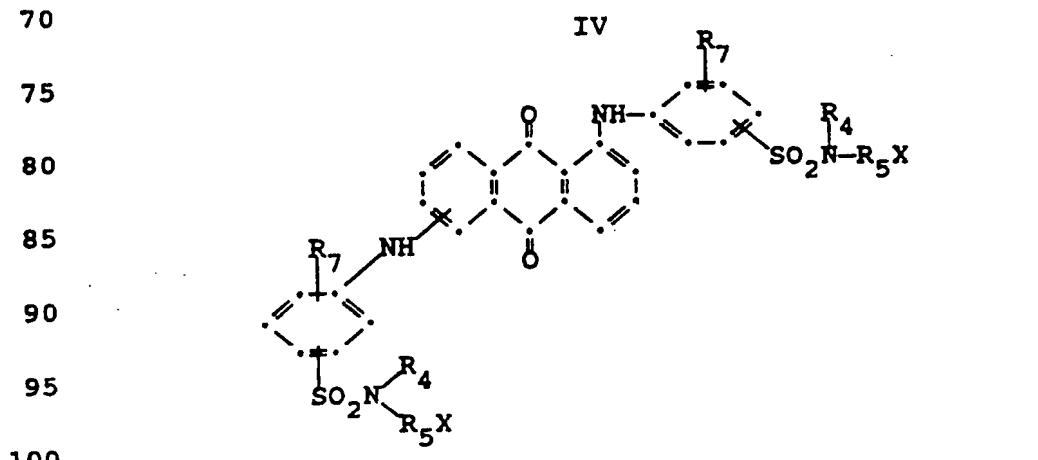
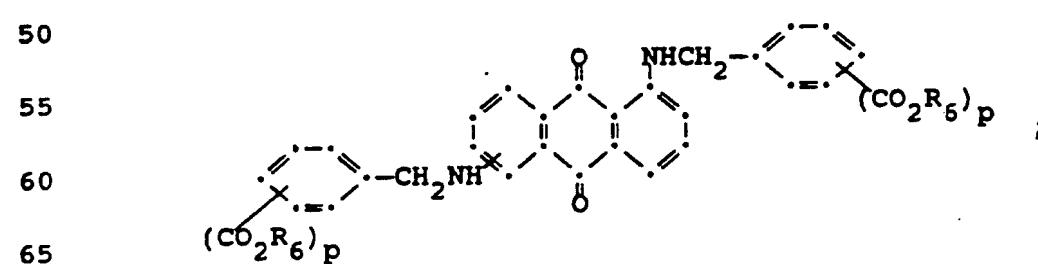
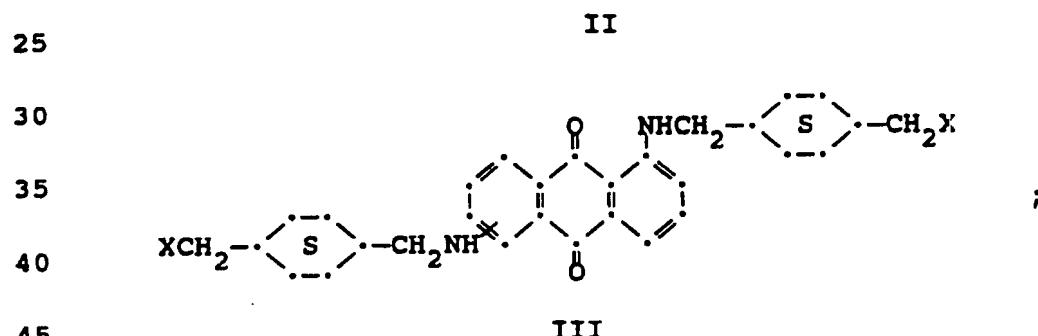
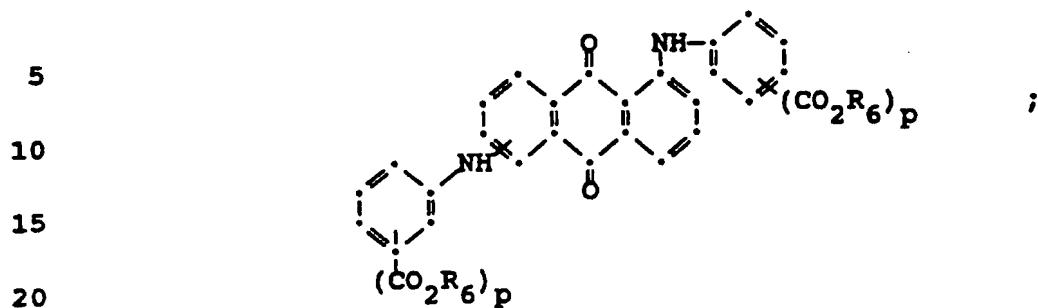
$R_5$  is a linking group selected from the group consisting of  $C_1-C_8$ -alkylene,  $C_1-C_6$ -alkylene-Z- $C_1-C_6$ -alkylene, arylene- $C_1-C_6$ -alkylene, arylene-Z- $C_1-C_6$ -alkylene,  $C_3-C_7$ -cycloalkylene,  $C_1-C_6$ -alkylene-cyclo-alkylene- $C_1-C_6$ -alkylene,  $C_1-C_6$ -alkylene-arylene- $C_1-C_6$ -alkylene, and  $C_1-C_6$ -alkylene-Z-arylene-Z- $C_1-C_6$ -alkylene, wherein Z is selected from -0-, -S- or  $SO_2$ ;

30

X is hydrogen or a polyester reactive group; and m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present.

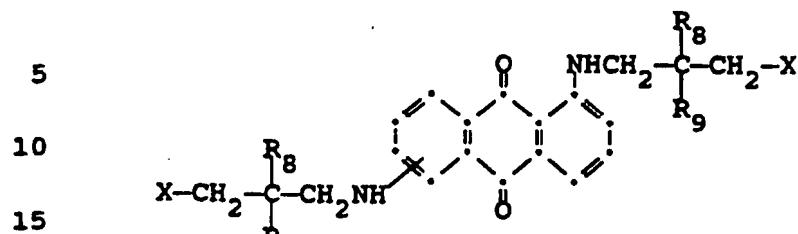
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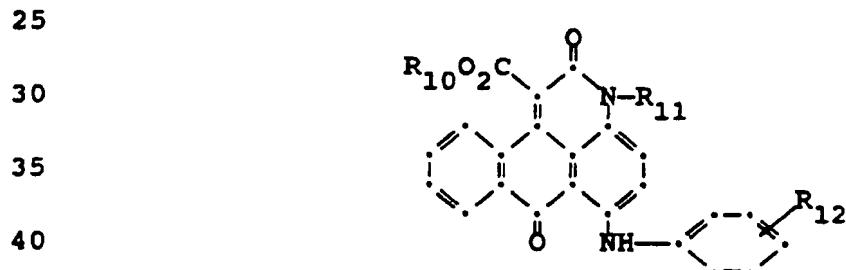


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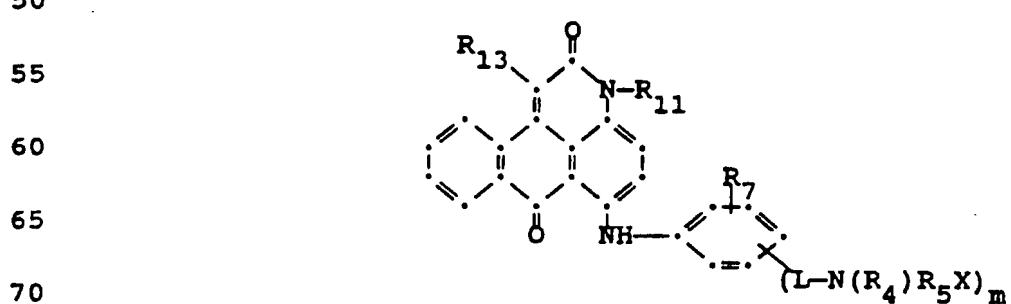
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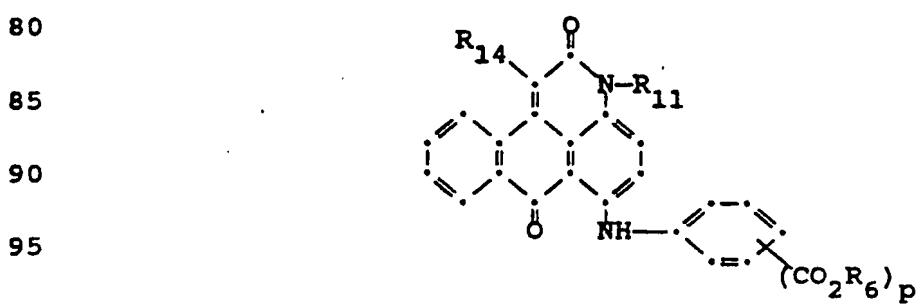
VI



VII



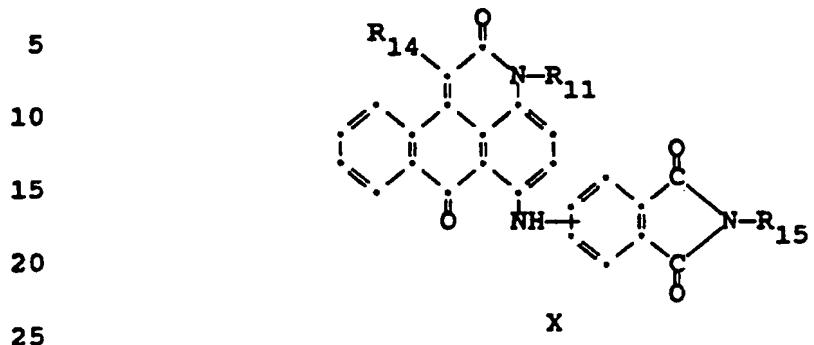
VIII



; and

IX

- 16 -



wherein:

30 R<sub>6</sub> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, substituted C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>3</sub>-C<sub>7</sub>-cycloalkyl or aryl;

R<sub>7</sub> is hydrogen or one to three groups selected from C<sub>1</sub>-C<sub>6</sub>-alkyl, substituted C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub>-alkanoylamino, halogen, hydroxy C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-alkylthio;

35         $R_8$  and  $R_9$  are the same or different and are selected from the group consisting of  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$ -alkyl,  $C_3-C_7$ -cycloalkyl or aryl;

$R_{10}$  is selected from the group consisting of  $C_1-C_6$ -alkyl,  $C_3-C_7$ -cycloalkyl or aryl;

40         $R_{11}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{12}$ -alkyl, substituted  $C_1$ - $C_{12}$ -alkyl,  $C_3$ - $C_7$ -cycloalkyl and aryl;

R<sub>12</sub> is hydrogen or one to three groups selected from the group consisting of C<sub>1</sub>-C<sub>6</sub>-alkyl, substituted C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-alkoxy, substituted C<sub>1</sub>-C<sub>6</sub>-alkoxy, C<sub>1</sub>-C<sub>6</sub>-alkylthio, substituted C<sub>1</sub>-C<sub>6</sub>-alkylthio, halogen, hydroxy, C<sub>1</sub>-C<sub>6</sub>-alkanoylamino, arylamino, C<sub>1</sub>-C<sub>6</sub>-alkylsulfonylamino and arylsulfonylamino;

50  $\text{CO}_2\text{R}_{10}$ ;  $\text{R}_{13}$  and  $\text{R}_{14}$  are selected from hydrogen, cyano or

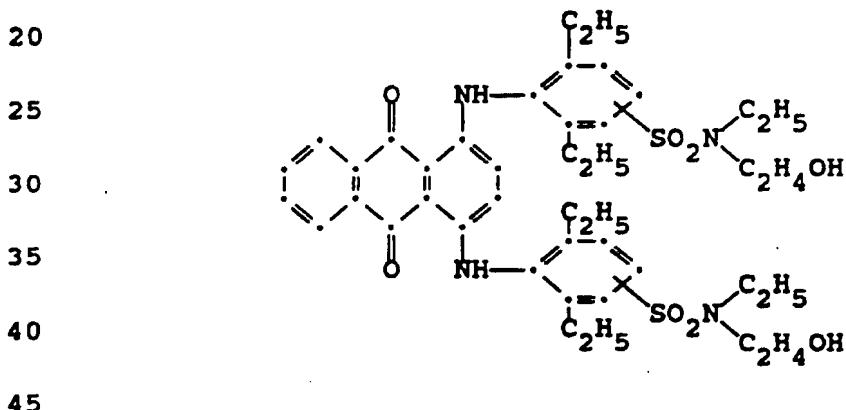
$R_{15}$  is  $R_4$  or  $R_5X$  as previously defined;

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L is  $-CO-$  or  $-SO_2-$ ; X is as previously defined; m is 0 or 1; p is 1 or 2; with the provisos that  $R_{13}$  is hydrogen when m is 0 and at least one polyester reactive group is present.

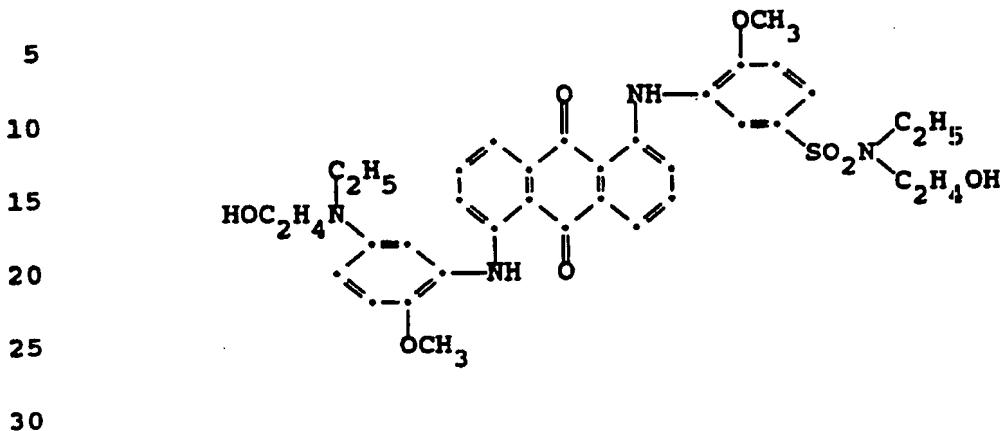
5        In a preferred embodiment, the blue anthraquinone compound(s) correspond to structure (I) above, wherein R is hydrogen;  $R_1$  and  $R_2$  are independently selected from methyl and ethyl;  $R_3$  is hydrogen, methyl, or bromo;  $R_4$  is hydrogen,  $C_1-C_4$ -alkyl or aryl;  $R_5$  is selected from 10 the group consisting of  $C_1-C_6$ -alkylene,  $C_1-C_4$ -alkylene- $O-C_1-C_4$ -alkylene,  $-CH_2C_6H_{10}CH_2-$ , arylene, or  $-CH_2$ -alkylene- and the red component corresponds to formula (V), wherein  $R_7$  is  $C_1-C_6$ -alkoxy and  $R_4$  and  $R_5$  are as defined in claim 1.

15        In an especially preferred embodiment of the present invention, the blue compound of formula (I) is



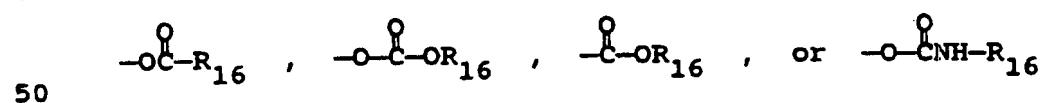
and the red compound of formula (V) is

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In a further preferred embodiment, the concentration of blue and red compounds taken together is from about 0.5 ppm to about 10 ppm. Most preferably, the total concentration of blue compound is 1 to 7 ppm and total concentration of red compound is 0.5 to 3 ppm.

40 The term "polyester reactive group" is used herein to describe a group which is reactive with at least one of the functional groups from which the polyester is prepared under polyester forming conditions. Examples of the groups which X may represent include hydroxy, carboxy, an ester group, amino,  $C_1-C_6$ -alkylamino, etc. The ester radicals may be any radical having the formulae



55 wherein  $R_{16}$  is selected from the group consisting of  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$ -alkyl,  $C_3-C_7$ -cycloalkyl or aryl. Reactive group X is preferably hydroxy, carboxy,  $C_1-C_2$ -alkoxycarbonyl or acetoxy.

In the terms "substituted  $C_1-C_6$ -alkyl", "substituted  $C_1-C_{12}$ -alkyl", "substituted  $C_1-C_6$ -alkoxy", "substituted  $C_1-C_6$ -alkylthio", "substituted  $C_1-C_6$ -alkylsulfonyl", "C<sub>1</sub>-C<sub>6</sub>-alkylsulfonylamido", "substituted

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alkylene", " $C_1-C_6$ -alkoxycarbonyl", the alkyl and alkylene groups or portions of the groups may contain as further substituents one or more groups, preferably one to three groups selected from the group consisting of

5      hydroxy, halogen, cyano, aryl, aryloxy, arylthio,  $C_1-C_4$ -alkylthio,  $C_1-C_4$ -alkylthio,  $C_3-C_7$ -cycloalkyl,  $C_1-C_4$ -alkanoyloxy and  $-(-O-R_{17}-)_p-R_{18}$ , wherein  $R_{17}$  is selected from the group consisting of  $C_1-C_6$ -alkylene,  $C_1-C_6$ -alkylenearylene, cyclohexylene, arylene, and

10      $C_1-C_6$ -alkylenecyclohexylene;  $R_{18}$  is selected from the group consisting of hydrogen, hydroxy, carboxy,  $C_1-C_4$ -alkanoyloxy,  $C_1-C_4$ -alkoxycarbonyl, aryl, and  $C_3-C_7$ -cycloalkyl; and  $p$  is 1, 2, 3, or 4.

15     The term "aryl" as used herein preferably denotes phenyl and phenyl substituted with one to three substituents selected from the group consisting of  $C_1-C_6$ -alkyl,  $C_1-C_6$ -alkoxy, halogen, carboxy, cyano,  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylsulfonyl, trifluoromethyl, hydroxy,  $C_1-C_6$ -alkanoyloxy,  $C_1-C_6$ -alkanoylamino, and  $C_1-C_6$ -alkoxycarbonyl.

20     The term "arylene" includes 1,2-, 1,3- and 1,4-phenylene and such radicals substituted one to three times with  $C_1-C_6$ -alkyl,  $C_1-C_6$ -alkoxy,  $C_1-C_6$ -alkoxy-carbonyl, or halogen.

25     The terms " $C_3-C_8$ -alkenyl" and " $C_3-C_8$ -alkynyl" are used to denote aliphatic hydrocarbon moieties having 3-8 carbons and containing at least one carbon-carbon double bond and one carbon-carbon triple bond, respectively.

30     The term "halogen" is used to indicate bromine, chlorine, fluorine, and iodine.

The terms " $C_1-C_6$ -alkanoyloxy" and " $C_1-C_6$ -alkanoyl-amino" are used to represent radicals of the formulae

35      $R_{19}-\overset{\text{O}}{\underset{\text{C}}{\text{O}}}-\text{O}-$     and     $R_{19}-\overset{\text{O}}{\underset{\text{C}}{\text{O}}}-\text{N}(\text{R}_6)-$  , respectively,

- 20 -

5 wherein  $R_{19}$  is a straight or branched chain  $C_1$ - $C_6$ -alkyl radical and  $R_6$  is as defined above.

Thus, the present invention provides a molding or fiber grade polyester preferably having copolymerized therein, in an amount sufficient to improve the apparent 10 whiteness and/or clarity of the polyester, a blue 1,4-bis(2,6-dialkylanilino)anthraquinone compounds of Formula (I) plus a red anthraquinone or anthrapyridone compounds of formulae (II) - (X) above. In this regard, the blue and red compounds will not be present in an 15 amount sufficient to impart a substantial amount of color to the polyester.

The organic toners may be added before the esterification, transesterification or polycondensation steps. As a further aspect of the present invention, 20 the method provided herein also involves the step of imparting clarity to the poly(ethylene terephthalate) or modified poly(ethylene terephthalate) of the invention.

In yet another aspect of the invention, there is provided in the method of polymerization, in the melt, 25 of an aromatic polycarboxylic acid or anhydride with a glycol using titanium compound catalysts to form high molecular weight linear polymers, the improvement comprising

(a) esterifying the acid or anhydride with the 30 glycol in the presence or absence of from about 1 ppm of Ti to about 50 ppm of Ti as an alkyl titanate at a temperature of between about 197°C and about 300°C. for a period of from about 0.5 hours to about 7 hours at a 35 pressure of between about 0 psig and about 100 psig at a molar ratio of glycol to acid or anhydride of about 1.1:1 to about 3:1,

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5 (b) further reacting and polycondensing the product of step (a) which contains the above mentioned titanium catalyst, in contact with a phosphorus based compound at about 1 to about 100 ppm phosphorus at a temperature of from about 250 to 310°C, under vacuum of from about 0.1 Torr to about 200 Torr for a period of from about 0.5 hour to 12.0 hours while removing the products of condensation so that

10 the resulting polymer has an intrinsic viscosity between about 0.4 to about 1.2 and contains less than 5 percent by weight diethylene glycol, without adding a diethylene glycol inhibitor, with each of the parts of

15 the compound being per million parts of the first polymer product and

20 (c) further polycondensing the crystallized product of step (b) in the solid-state and in the presence of countercurrent inert gas or under vacuum and at elevated temperatures of from about 200°C to about 235°C for 2 - 24 hours.

25 Molded articles or fibers can be prepared from the product of the invention. Containers are the preferred molded article.

30 As noted above, the toner blends of the present invention can be added before or during polymerization.

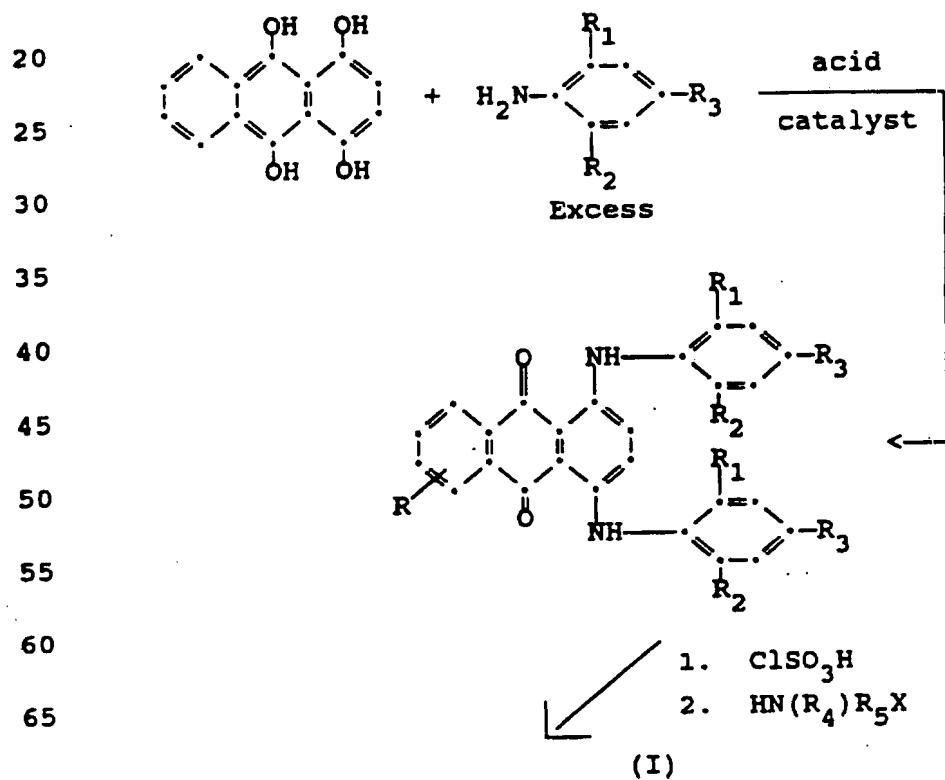
35 Accordingly, as a further aspect of the present invention, there is provided a premix composition comprising a blend of at least one blue 1,4-bis(2,6-dialkylanilino)anthraquinone compound of formula (I), along with a red anthraquinone or anthrapyridone compound of formulae (II) - (X) above. The premix composition may be a neat blend of the red and blue compounds or the composition may be

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pre-dissolved in one of the polyester's monomeric species, e.g., ethylene glycol.

The total amount of toner components added depends, of course, on the amount of inherent yellow color in the polyester. Generally, a maximum concentration of about 10 ppm of combined toner components and a minimum concentration of about 0.5 ppm are required with about 1 - 7 ppm of blue component (I) in combination with about 0.5 - 3 ppm of red components of formulae (II - X) being preferred.

The blue anthraquinones of formula (I) can be prepared in general by reaction of leuco quinizarin (1,4,9,10-tetrahydroxyanthracene) compounds with an excess of aromatic amines, preferably in the presence of acid catalysts such as boric acid as described in U.S. Patent No. 3,918,976, incorporated herein by reference and as follows:



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The 1,4-bis(2,6-dialkylanilino)anthraquinone compounds thus produced are readily functionalized if needed by first chlorosulfonating with chlorosulfonic acid to produce di-sulfonyl chlorides which can be reacted with amines containing polyester reactive groups, the general method being disclosed in U.S. Patent No. 2,731,476, incorporated herein by reference.

Typical amines corresponding to formula  $\text{HN}(\text{R}_4)\text{R}_5\text{X}$  include 2-aminoethanol, 2,2-iminodiethanol, 1-amino-2,3-propanediol, 2-methylaminoethanol, 2-ethylaminoethanol, 2-anilinoethanol, methyl anthranilate, methyl m-amino benzoate, p-aminobenzoic acid, m-aminophenol, 6-amino-hexanoic acid,  $\beta$ -alanine, glycine ethyl ester, 2-(p-aminophenyl)ethanol, 2-(p-aminophenoxy)ethanol 4-aminomethylcyclohexane methanol and 3-amino-2,2-dimethyl-1-propanol.

Red compounds (II) can be prepared by reacting 1,5-dichloroanthraquinone and/or 1,8-dichloroanthraquinone or mixtures thereof with o, m- and p-aminobenzoic acids (and esters thereof) by a modified Ullmann reaction involving nitrogen arylation of the anilines in the presence of copper catalysts (see U.S. Patent No. 4,359,580, incorporated herein by reference).

Red compounds of formula (III) can be prepared as described in U.S. Patent No. 4,420,581 and compounds of formula (VI) can be prepared as in U.S. Patent No. 4,999,418, incorporated herein by reference.

Red anthraquinone compounds of formula (IV) can be prepared by reacting 1,5-dichloroanthraquinone and 1,8-dichloroanthraquinone or mixtures thereof with substituted benzyl amines by procedures similar to those used in preparing compounds of formulae (III) and (VI).

Red anthrapyridone compounds (VII) can be prepared as disclosed in U.S. Patent No. 4,790,581 incorporated

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herein by reference; procedures useful in preparing red-violet anthrapyridone compounds (VIII) and (IX) are disclosed in U.S. Patent No. 4,745,174, incorporated herein by reference.

5 Haze half-times are defined as the time after the start of crystallization of a material when the level of haze becomes such that the amount of light transmitted through a film of the sample reaches half of its maximum value. This halftime is roughly the same as the 10 crystallization half-times known in the art. Examples of measurements of crystallization half-times are disclosed in J. Polymer Sci. A2, Vol. 6 (1962) by Adams and Stein.

15 A haze half time test has been found to be useful in determining haze results in molded preforms. It has been found to be an excellent measure of crystallization rate with respect to bottle polymer applications. Polymers with higher haze half times are less likely to contain haze in preforms. In this test, a hazemeter is 20 used to measure the light absorbance of a molten polymer film as it crystallizes and becomes more turbid (hazy); the resulting turbidity verses time data are analyzed to obtain a half time. The haze half time test has been used to measure the crystallization rate in the 25 experimental section as follows below. This invention involves a process for preparing polyesters having a slow crystallization rate, using TPA as the primary source of the terephthalate moiety, long melt phase polycondensation times, and a catalyst system as 30 described herein.

The haze half-times referred to in the following examples are measured by method described as follows:

35 The polymer sample (a fine powder) is melted for about 20 seconds between 2 aluminum blocks heated to about 280°C. The sample is transferred to a set of 2

- 25 -

aluminum blocks heated to about 130°C. Light is transmitted from a projector lamp which is sent through the sample as it crystallizes isothermally and the light intensity is measured using a photodetector. The 5 photodetector signal is recorded using a computer and is analyzed to determine the time after the start of crystallization when the level of haze becomes such that the amount of light transmitted through a film of the sample reaches half of its maximum.

10 Polymer prepared using this process has a significantly higher haze half time than polymer prepared by conventional processes such antimony (Sb) based catalyst combined with phosphorus (see attached Table 1). Polymer prepared by the process described in 15 this invention is useful for obtaining poly(ethylene terephthalate) or modified poly(ethylene terephthalate) with a slow crystallization rate for molding haze free preforms which are used to blow mold bottles of different sizes.

20 This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless 25 otherwise specifically indicated. The starting materials are commercially available unless otherwise indicated.

#### EXAMPLES

30 **Example 1** - Preparation of Terephthalic Acid (TPA) Based Oligomer

Ethylene glycol (450 lbs) was placed in a paste preparation vessel. The agitator of the vessel was started. TPA powder (1050 lbs) was added slowly at a 35 rate of 30 lbs/min. The paste was allowed to circulate

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for 1 hr with a heating loop on the vessel maintained at 40°C to obtain a slurry. The slurry was feed at a rate of 4 lbs/hr to obtain a total feed of 493 lbs into an esterification vessel which contained a heat from a 5 previous run and was at 250°C. This vessel was equipped with a stirrer and a low boiler column to collect distillates. The temperature was ramped from 250°C to 265°C in 1 hr after feeding all of the ethylene glycol/TPA slurry. The pressure of the vessel was built 10 to 25 psig and maintained. The esterification reaction was allowed to proceed until the level of water in the low boiler column was at a steady state. A portion of the final oligomer was dumped into metal cans and 15 allowed to cool. The final oligomer was ground to 3 to 5 mm particle size. The oligomer had an acid number of 5.40 and was found by analysis to contain 71.43 equivalents carboxyl per million grams. The  $M_n$  by GPC was 953 and the  $M_w$  by GPC was 1470.

20

Example 2 - Preparation of PET Precursor Using Sb/P Catalyst

25 The following materials were placed in a stainless steel reactor equipped with a nitrogen inlet, stirrer, and vacuum outlet.

1090 g TPA based oligomer described in Example 1  
30 0.0029 g 1-cyano 6-[4'-(2-hydroxyethyl)anilino]-3H-dibenz[f,ij]isoquinoline-2,7-dione  
0.0318 g antimony trioxide  
35 10.2 ml of an ethylene glycol slurry of mixed phosphorus ester compositions (Merpol A) containing 0.07488 g phosphorus  
1.4 g of diethylene glycol (2,2'-oxydiethanol)

40

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The temperature of the reactor and contents was elevated from room temperature to 280°C over a 70 minute time interval with a nitrogen sweep over the reaction mixture. Stirring was begun when the internal 5 temperature of the reaction had reached 220°C. Vacuum was applied at 280°C. The pressure was reduced to 200 torr and was held at 200 torr for 10 minutes. The pressure was reduced to 2.5 torr and the melt phase polycondensation reaction was completed by heating at 10 2.5 torr for 3 hours. The polymer was extruded from the reactor through ice water in a metal trough into a pelletizer to obtain polymer pellets. The pelletized polymer had an inherent viscosity of 0.57 dL/g and was shown by analysis to contain 2 wt % diethylene glycol 15 (DEG).

20 Example 3 - Solid State Polycondensation of poly(ethylene terephthalate) (PET) from Example 2

PET polymer pellets (160 g) from Example 2 were crystallized in a 180°C air oven for 45 minutes. The crystallized pellets were placed in a solvent heated 25 glass solid stating apparatus with the nitrogen flow set at 14 SCFH (standard cubic feet per hour). Methyl salicylate was used as the refluxing solvent to yield a solid stating temperature of 222°C to 223°C. The pellets were allowed to polycondense in the solid state 30 for 3 hrs and 25 min. The resulting polymer had an inherent viscosity of 0.72 dL/g and haze half times of 65 and 70 seconds on duplicate samples.

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Example 4 - Preparation of PET Precursor Using Ti/P Catalyst

The following materials were placed in a stainless steel reactor equipped with a nitrogen inlet, stirrer, and vacuum outlet.

10 1090 g TPA based PET oligomer described in Example 1

15 0.0029 g 1-cyano 6-[4'-(2-hydroxyethyl)anilino]-3H-dibenz[f,ij]isoquinoline-2,7-dione

1.95 g diethylene glycol

20 0.16 ml acetyltriisopropyl titanate in butanol containing 0.0048 g of Ti

0.6 ml of an ethylene glycol slurry of a mixed ester composition (Merpol A) containing 0.0048 g P

25 The heating, polycondensation, and pelletization were done as described in Example 2 except the final melt phase polycondensation stage was done at 3.25 torr for 3 hours. The final pelletized polymer had an inherent viscosity of 0.58 dL/g and was shown by analysis to contain 1.87 wt % DEG.

30 Example 5 - Solid State Polycondensation of PET from Example 4

PET polymer pellets (160 g) from Example 4 were crystallized and allowed to polycondense in the solid state as described in Example 3 except the solid state polycondensation was done for 4 hours and 39 minutes. The resulting polymer had an inherent viscosity of 0.71 dL/g and haze half times of 126 and 132 seconds on duplicate samples.

40 As shown in Table I, polymers prepared by the process described in this invention is useful for

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obtaining a poly(ethylene terephthalate) based polyester with a slow crystallization rate for molding haze preforms which are used to blow mold bottles of different sizes.

5

TABLE 1

Haze Half Times of PET Polymers<sup>a</sup>

	Example Number	Catalyst System <sup>b</sup> (ppm)	Haze Half Time <sup>c</sup> (seconds)
10	Example 3	227 Sb, 78 P	65, 70
15	Example 5	5 Ti, 6 P	126, 132

20 (a) The PET polymers are terephthalic acid based and were prepared using a melt phase polycondensation time of 3 hrs.

(b) The catalyst levels contained in the polymers were determined by X-ray fluorescence analysis.

25 (c) PET polymers with higher haze half times show less propensity for haze when bottle preforms are molded.

- 30 -

CLAIMS

We claim:

- 5        1. A process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising:  
10                reacting a diacid component further comprising at least 65 mole % terephthalic acid or a diester component comprising at least 65 mole % C<sub>1</sub> - C<sub>4</sub> dialkyl terephthalate and a diol component comprising at least 65 mole % ethylene glycol at temperatures to effect steps (A) and (B) as  
15                follows:  
              (A)        esterification or transesterification, wherein said esterification is carried out,  
20                optionally, in the presence of about 1 to about 50 parts of titanium present in the form of an alkyl titanate or  
              optionally, in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid, and  
25                wherein said transesterification is carried out in the presence of from about 1 to about 50 parts of titanium in the form of an alkyl titanate; and  
30                wherein said transesterification is carried out in the presence of from about 1 to about 50 parts of titanium in the form of an alkyl titanate; and

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(B) polycondensation, wherein said polycondensation is carried out in the presence of a catalyst system comprising from about 1 to about 50 parts of titanium present in the form of an alkyl titanate and from about 1 to about 100 parts of phosphorus in the form of a phosphate ester or phosphoric acid;

5 each of the parts of the catalyst representing per million parts of polymer product, wherein the mole percentage for all of the diacid component totals 100 mole %, and wherein the mole percentage for all of the diol component totals 100 mole %.

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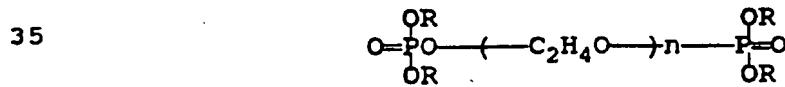
15 2. The process of Claim 1 wherein said diacid component comprises at least 95 mole % terephthalic acid and the diol component comprises at least 95 mole % ethylene glycol.

20 3. The process of Claim 1 wherein said diacid component is terephthalic acid and said diol component is ethylene glycol.

25 4. The process of claim 1 wherein said alkyl titanate is acetyl triisopropyl titanate.

5. The process of claim 1 wherein said phosphorus-based compound is a phosphate ester.

30 6. The process of Claim 5 wherein said phosphate ester has the formula



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5       wherein n has an average value of 1.5 to about 3.0 and each R is selected from the group consisting of hydrogen or an alkyl radical having from 6 to 10 carbon atoms, wherein the ratio of the number of R groups or hydrogen atoms to the number of phosphorus atoms being from about 0.25 to about 0.50 and the ester having a free acidity equivalent of about 0.2 to 0.5.

10

15       7. The process of Claim 5 wherein said phosphate esters comprise ethyl acid phosphate, diethyl acid phosphate, triethyl acid phosphate, arylalkyl phosphates, tris-2-ethylhexyl phosphate and mixtures thereof.

20       8. The process of Claim 1 wherein said phosphorus compound is phosphoric acid.

25       9. The process of Claim 1 wherein said catalyst system comprises above 1 to about 20 parts of catalyst metal in the form of alkyl titanate and from about 1 to about 50 phosphorus in the form of said phosphorus compound.

30       10. The process of Claim 1 wherein said catalyst system comprises about 3 to about 10 parts of catalyst metal in the form of an alkyl titanate and from about 5 to about 15 parts of phosphorus in the form of said phosphorus-based compound.

35       11. The process of Claim 1 wherein said catalyst system further comprises an inorganic toner.

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12. The process of Claim 11 wherein said toner further comprises salts of cobalt.
- 5 13. The process of Claim 11 wherein said salt of cobalt is cobalt acetate.
- 10 14. The process of Claim 13 wherein said cobalt acetate is present in the amount of 10-120 ppm Co, the acetyl triisopropyl titanate is present in the amount of 1-50 ppm Ti, and the phosphorus-based compound is present in the amount of 1-100 ppm P, all parts by weight based on the total weight of the polymer.
- 15 15. A process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.65 dL/g comprising reacting
  - 20 (a) a diacid or diester component comprising at least 65 mole % terephthalic acid or C<sub>1</sub> - C<sub>4</sub> dialkyl terephthalate,
  - (b) a diol component comprising at least 65 mole % ethylene glycol, and
  - (c) an organic toner system comprising about 1 to about 10 ppm of at least one copolymerizable 6-aryl amino -1-cyano-3H-dibenz [f,ij] isoquinoline-2,7-dione or at least one copolymerizable 1,4-bis(2,6-dialkylanilino) anthraquinone compound in combination with at least one copolymerizable anthraquinone or red anthrapyridone (6-aryl amino-3H-dibenz[f,ij] isquinoline-2,7-dione) compound at temperatures to effect steps (A) and (B) as follows:(A) esterification or transesterification, wherein said esterification is carried out,
- 25
- 30
- 35

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optionally, in the presence of about 1 to  
about 50 parts of titanium present in the form  
of an alkyl titanate or optionally, in the  
presence of a catalyst system comprising from  
about 1 to about 50 parts of titanium present  
in the form of an alkyl titanate and from  
about 1 to about 100 parts of phosphorus in  
the form of a phosphate ester or phosphoric  
acid, and

5

10

wherein said transesterification is carried  
out in the presence of from about 1 to about  
50 parts of titanium in the form of an alkyl  
titinate; and

15

(B) polycondensation, wherein said  
polycondensation is carried out in the  
presence of a catalyst system comprising from  
about 1 to about 50 parts of titanium present  
in the form of an alkyl titanate and from  
about 1 to about 100 parts of phosphorus in  
the form of a phosphate ester or phosphoric  
acid;

20

each of the parts of the catalyst representing  
per million parts of polymer product, wherein the  
mole percentage for all of the diacid component  
totals 100 mole %, and wherein the mole percentage  
for all of the diol component totals 100 mole %;  
wherein at least one polyester reactive group is  
present on each toner component used.

25

30

16.

The process of Claim 15 where the diacid or diester  
component comprises at least 95 mole % terephthalic  
acid or C<sub>1</sub>-C<sub>4</sub> dialkyl terephthalate or mixtures  
thereof and the diol component comprises at least  
95 mole % ethylene glycol.

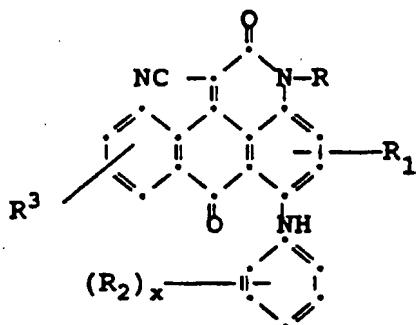
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- 35 -

17. The process of Claim 15 wherein the diacid component is terephthalic acid and the diol component is ethylene glycol.

5 18. The process at Claim 15 wherein the toner comprises at least one 6-arylamino-1-cyano-3H-dibenz [f,ij] isoquinoline-2,7-diones having the formulae

10  
15  
20  
25  
30



wherein

35 R is hydrogen, cycloalkyl, allyl, alkyl, aryl, aralkyl, alkoxyalkyl or cycloalkylalkylene;

R<sub>1</sub> is hydrogen, halogen, alkyl, alkoxy, aryloxy, alkylthio or arylthio;

40 R<sub>2</sub> is hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, alkylthio, arylthio, carbalkoxy, carbaryloxy, carbaralkoxy, carboxy, sulfamoyl, alkylsulfamoyl, dialkylsulfamoyl, alkylarylsulfamoyl, cycloalkylsulfamoyl, arylsulfamoyl, carbamoyl, alkylcarbamoyl, dialkylcarbamoyl, alkylarylcaramoyl, cycloalkylcarbamoyl, arylcarbamoyl, 2-pyrrolidono, acylamido, or N-alkylacylamido;

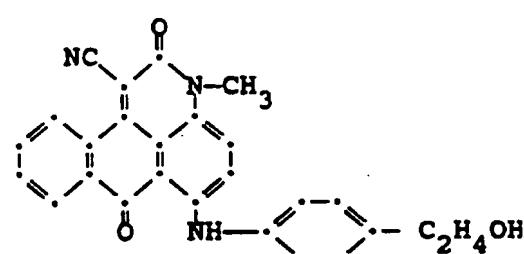
45 R<sub>3</sub> is one or more residues selected from the group consisting of hydrogen, halogen, alkyl and alkoxy; and

50

- 36 -

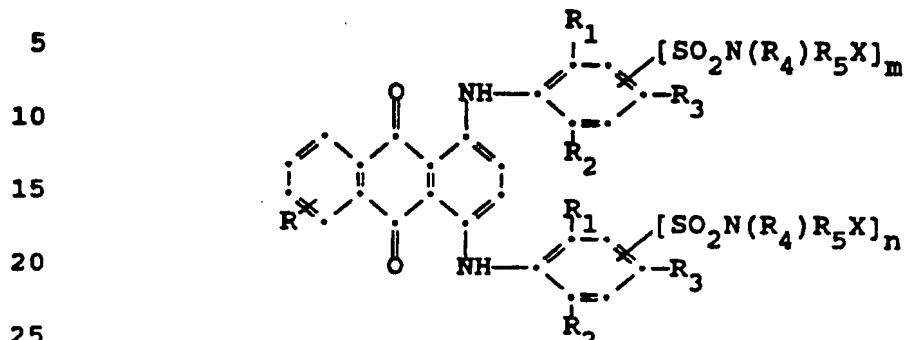
x is an integer of 1 to 5; wherein one or more of the alkyl, alkoxy, alkoxy, aryl, aryloxy, alkylthio, arylthio or aralkyl residues may contain one or more reactive groups selected from the group consisting of carboxy, carbalkoxy, carbaryloxy, N-alkyl-carbamoyloxy, carbamoyloxy, acyloxy, chlorocarbonyl, hydroxyl, cycloalkylcarbonyloxy, N-arylcarbamoyloxy and N,N-dialkylcarbamoyloxy and wherein said alkyl and aryl groups may contain substituents selected from the group consisting of alkoxy, acyloxy, cyano, hydroxy, halogen and acylamido; wherein at least one polyester reactive group is present to permit copolymerization.

19. The process of Claim 17 wherein the toner compound copolymerized is



20. The process of Claim 15 wherein said toner comprises at least one blue 1,4-bis(2,6-dialkylanilino) anthraquinone compound of Formula (I)

- 37 -



wherein:

R is selected from the group consisting of hydrogen,  $C_1-C_6$  alkyl, halogen, carboxy, and  $C_1-C_6$  alkoxy- $\overset{\text{O}}{\text{C}}-$ ;

40  $R_1$  and  $R_2$  are independently  $C_1-C_6$ -alkyl;  
 45  $R_3$  is selected from the group consisting of hydrogen, halogen,  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$  alkyl, hydroxy,  $C_1-C_6$ -alkoxy, substituted  $C_1-C_6$ -alkoxy, cyano, thiocyano,  $C_1-C_6$ -alkylthio, substituted  $C_1-C_6$ -alkylthio,  $C_1-C_6$ -alkylsulfonyl, substituted  $C_1-C_6$ -alkylsulfonyl,  $C_1-C_6$ -alkoxycarbonyl, carboxy, aryloxy, arylthio, arylsulfonyl, and  $SO_2N(R_4)R_5X$  when m and/or n are zero;

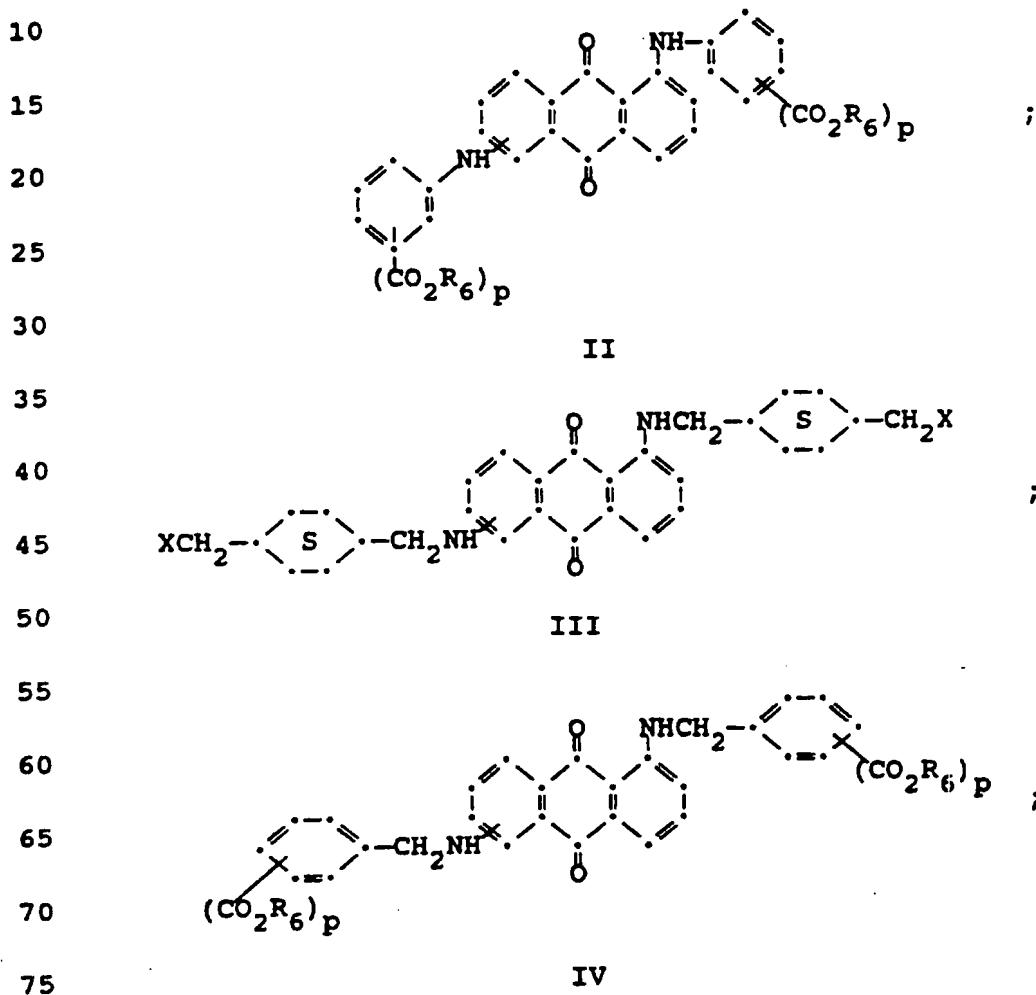
50  $R_4$  is selected from the group consisting of hydrogen,  $C_1-C_6$ -alkyl, substituted  $C_1-C_6$ -alkyl,  $C_3-C_8$ -alkenyl,  $C_3-C_8$ -alkynyl,  $C_3-C_7$ -cycloalkyl and aryl;

55  $R_5$  is a linking group selected from the group consisting of  $C_1-C_8$ -alkylene,  $C_1-C_6$ -alkylene- $Z-C_1-C_6$ -alkylene, arylene- $C_1-C_6$ -alkylene,  $C_3-C_7$ -cycloalkylene,  $C_1-C_6$ -alkylene-cyclo-alkylene- $C_1-C_6$ -alkylene,  $C_1-C_6$ -alkylene-arylene- $C_1-C_6$ -alkylene, and  $C_1-C_6$ -alkylene- $Z$ -arylene- $Z-C_1-C_6$ -alkylene, wherein Z is selected from  $-O-$ ,  $-S-$  or  $SO_2$ ;

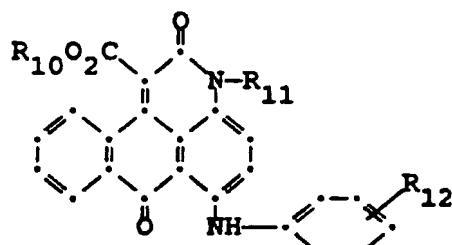
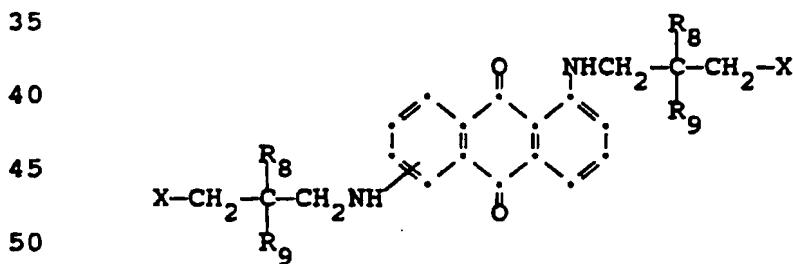
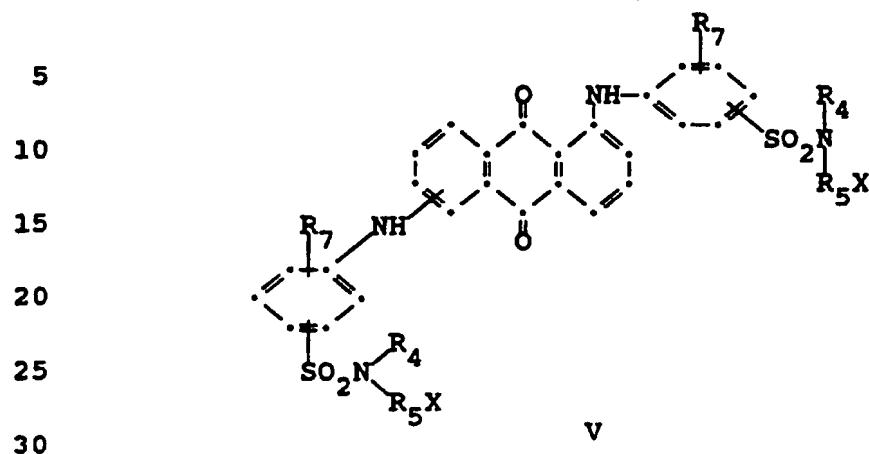
- 38 -

X is hydrogen or a polyester reactive group; and m and n are independently 0 or 1; with the proviso that at least one polyester reactive group is present;

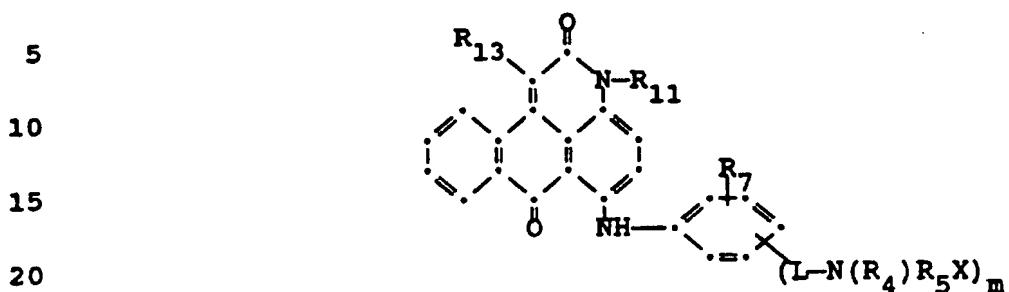
5 along with at least one red anthraquinone or anthrapyridone compound selected from formulae (II) - (X) below:



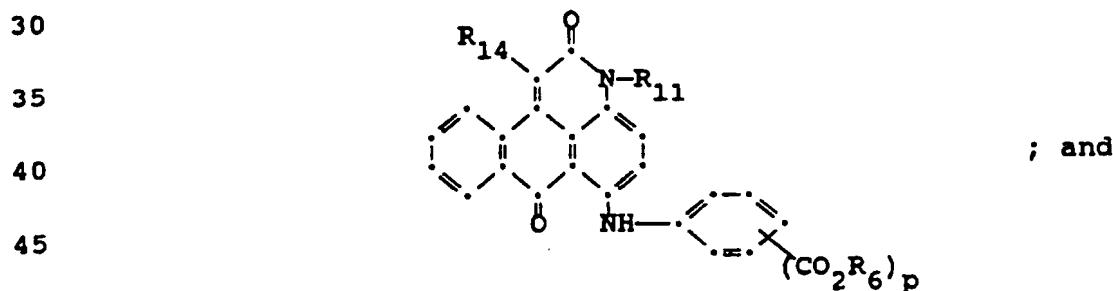
- 39 -



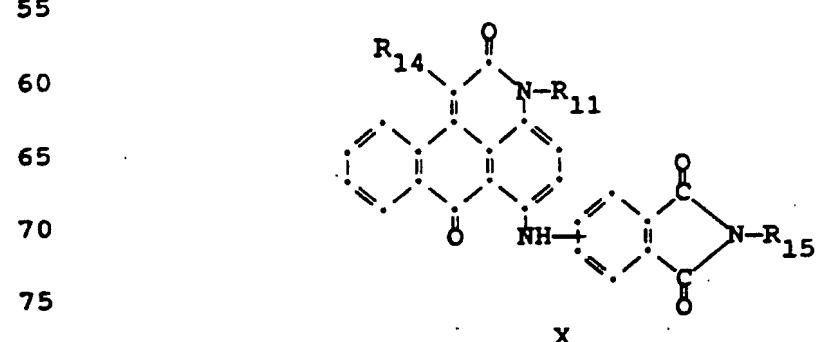
- 40 -



25 VIII



50 IX



30 *wherein:*

85 R<sub>6</sub> is selected from the group consisting of hydrogen, C<sub>1</sub>-C<sub>6</sub>-alkyl, substituted C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>7</sub>-cycloalkyl or aryl;

R<sub>7</sub> is hydrogen or one to three groups selected from C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>1</sub>-C<sub>6</sub>-substituted alkyl, C<sub>1</sub>-C<sub>6</sub>-

- 41 -

alkanoylamino, halogen, hydroxy  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -alkoxy,  $C_1$ - $C_6$ -alkylthio;

5         $R_8$  and  $R_9$  are the same or different and are selected from the group consisting of  $C_1$ - $C_6$ -alkyl, substituted  $C_1$ - $C_6$ -alkyl,  $C_3$ - $C_7$ -cycloalkyl or aryl;

$R_{10}$  is selected from the group consisting of  $C_1$ - $C_6$ -alkyl,  $C_3$ - $C_7$ -cycloalkyl or aryl;

10       $R_{11}$  is selected from the group consisting of hydrogen,  $C_1$ - $C_{12}$ -alkyl, substituted  $C_1$ - $C_{12}$ -alkyl,  $C_3$ - $C_7$ -cycloalkyl and aryl;

15       $R_{12}$  is hydrogen or one to three groups selected from the group consisting of  $C_1$ - $C_6$ -alkyl, substituted  $C_1$ - $C_6$ -alkyl,  $C_1$ - $C_6$ -alkoxy, substituted  $C_1$ - $C_6$ -alkoxy,  $C_1$ - $C_6$ -alkylthio, substituted  $C_1$ - $C_6$ -alkylthio, halogen, hydroxy,  $C_1$ - $C_6$ -alkanoylamino, aroylamino,  $C_1$ - $C_6$ -alkylsulfonylamino and arylsulfonylamino;

$R_{13}$  and  $R_{14}$  are selected from hydrogen, cyano or  $CO_2R_{10}$ ;

20

$R_{15}$  is  $R_4$  or  $R_5X$  as previously defined;

$L$  is  $-CO-$  or  $-SO_2-$ ;  $X$  is as previously defined;  $m$  is 0 or 1; and  $p$  is 1 or 2; with the provisos that  $R_{13}$  is hydrogen when  $m$  is 0 and at least one polyester reactive group is present.

21. The process of Claim 20 wherein the blue anthraquinone compound(s) correspond to said structure (I), wherein  $R$  is hydrogen;  $R_1$  and  $R_2$  are independently selected from methyl and ethyl;  $R_3$  is hydrogen, methyl, or bromo;  $R_4$  is hydrogen,  $C_1$ - $C_4$ -alkyl or aryl;  $R_5$  is selected from the group consisting of  $C_1$ - $C_6$ -alkylene,  $C_1$ - $C_4$ -alkylene- $O$ - $C_1$ - $C_4$ -alkylene,  $-CH_2C_6H_{10}CH_2-$ , 30      arylene, or  $-CH_2$ -arylene- and the red component

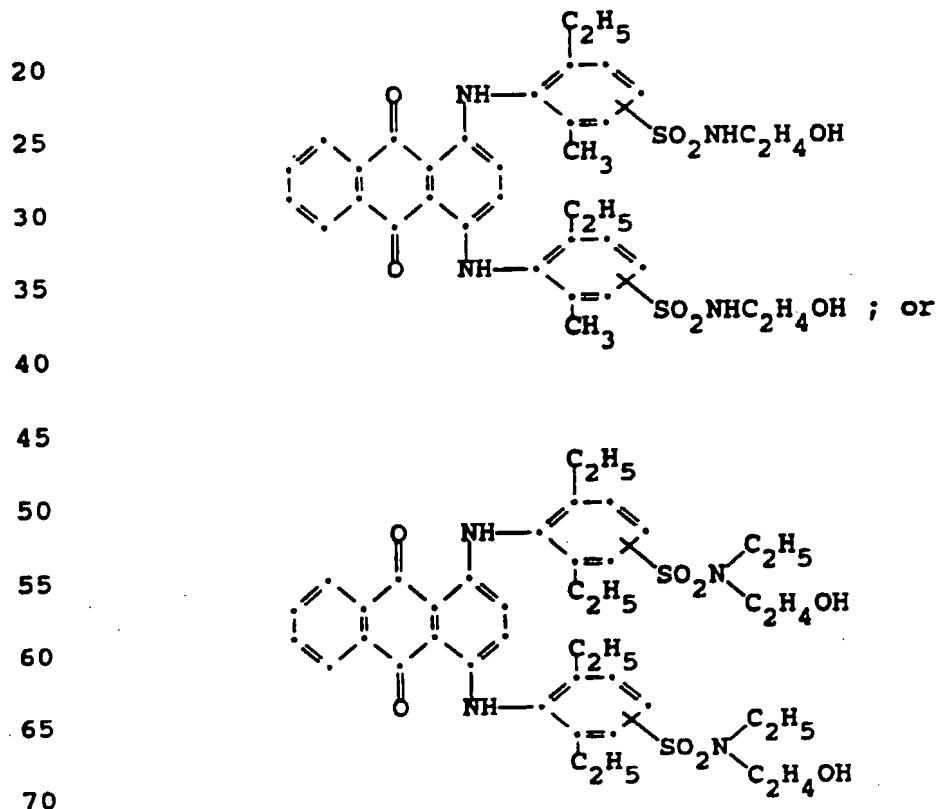
- 42 -

corresponds to formulae (V), wherein R<sub>7</sub> is C<sub>1</sub>-C<sub>6</sub>-alkoxy and R<sub>4</sub> and R<sub>5</sub> are as defined in Claim 19.

5        22. The process of Claim 21 wherein the concentration of blue and red compounds taken together is from about 1.0ppm to about 10ppm.

10       23. The process of Claim 21 wherein the total concentration of blue compound(s) is about 1 to 7ppm and the concentration of red compound(s) is about 1.0 to 3ppm.

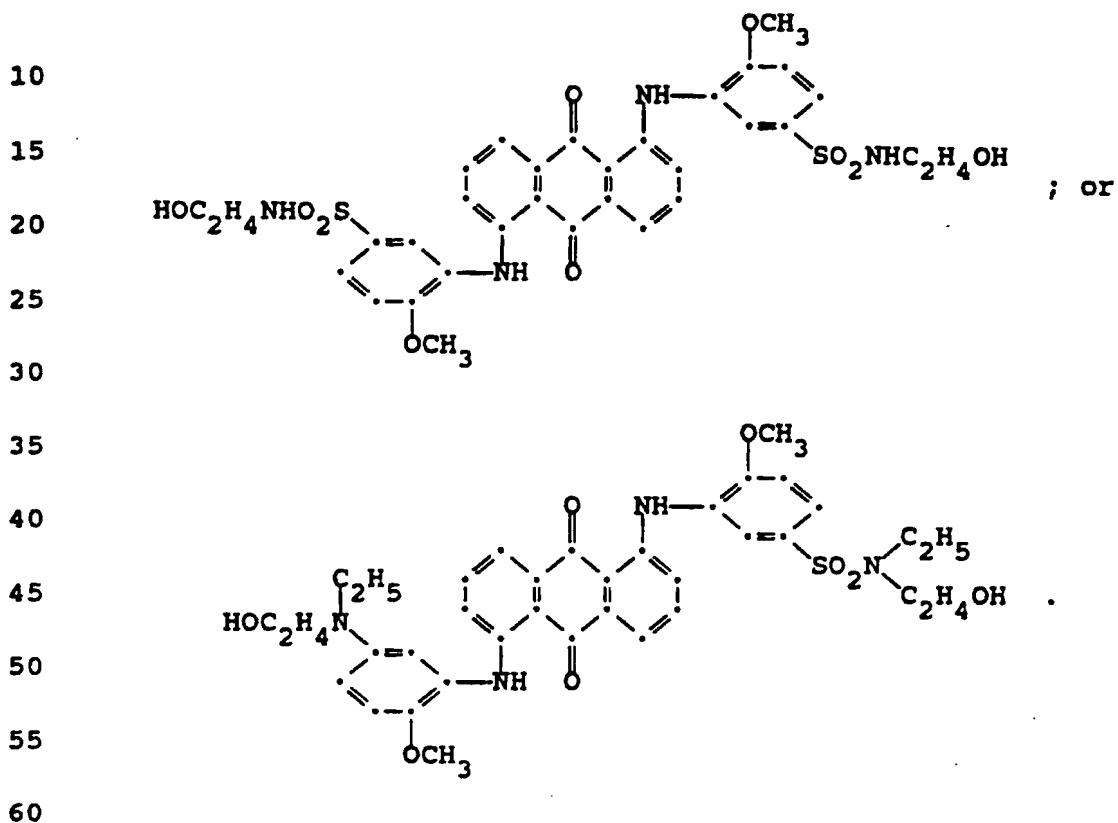
15       24. The polyester of Claim 21, 22, 23, or 24, wherein the compound of formula (I) is



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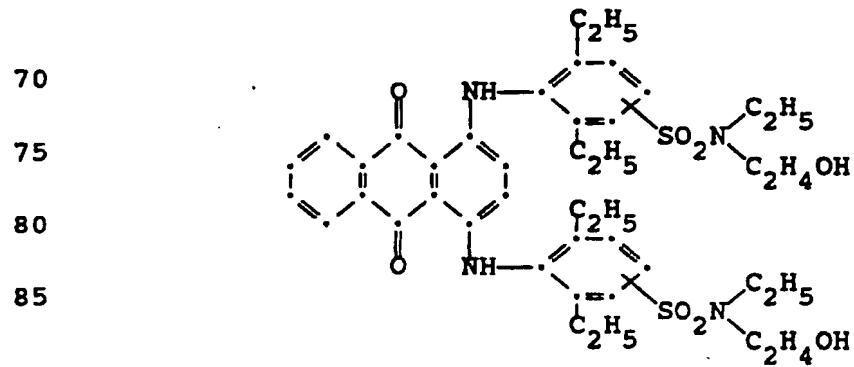
24. The polyester of Claim 20, 21, 22, 23, or 24  
wherein the red compound of formula (V) is

5



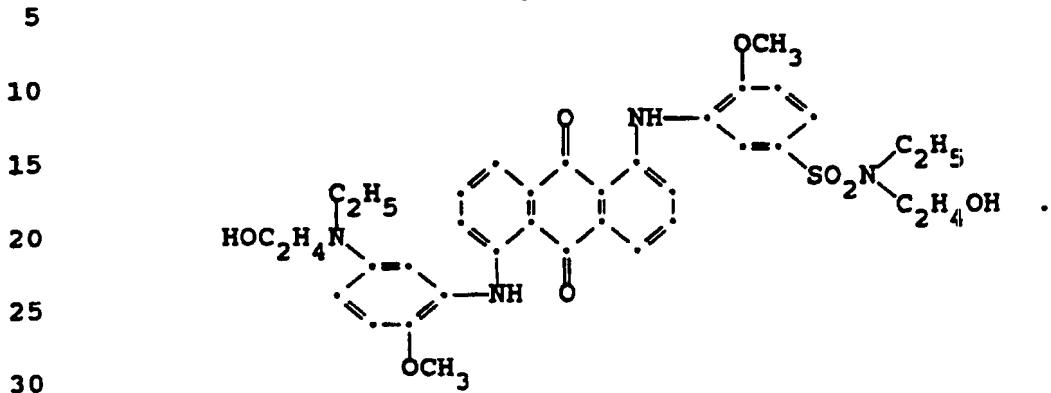
26. The polyester of any one of Claims 20, 21, 22, 23,  
24, 25 wherein the blue compound of formula (I) is

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and wherein the red compound of formula (V) is



- 45 -

about 197°C and about 300°C. for a period of from about 0.5 hours to about 7 hours at a pressure of between about 0 psig and about 100 psig at a molar ratio of glycol to acid or anhydride of about 1.1:1 to about 3:1,

5 (b) further reacting and polycondensing the product of step (a), which contains said titanium catalyst, in contact with a phosphorus based compound at about 1 to about 100 ppm phosphorus at a temperature of from about 250 to 310°C, under vacuum of from about 0.1 Torr to about 200 Torr for a period of from about 0.5 hour to 12.0 hours while removing the products of condensation so that 10 the resulting polymer has an intrinsic viscosity between about 0.4 to about 1.2 and contains less than 5 percent by weight diethylene glycol, without adding a diethylene glycol inhibitor, with each of the parts of 15 the compound being per million parts of the first polymer product and 20 (c) further polycondensing the crystallized product of step (b) in the solid-state and in the presence of an inert gas or under vacuum and at temperatures of from about 200°C to 25 about 235°C for 2 - 24 hours.

29. A product prepared by the process of Claim 1.

30 30. The product of Claim 29 which is clear.

31. A molded article prepared from moldable poly(ethylene terephthalate) made by the process of Claims 1, 10 and 14.

- 46 -

**32. The molded article of Claim 29 which is a container.**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/16378

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RESEARCH DISCLOSURE, vol. 167, no. 010, March 1978, HAVANT GB, page 4 XP002001216 ANONYMOUSLY: "Titanium catalyst for polyester synthesis" see the whole document ---	1-4, 8-14, 29-31
A	US,A,4 250 078 (MCFARLANE ET AL.) 10 February 1981 see claims 1-4; example 8 ---	1,11,15, 20-26
A	US,A,3 907 754 (TERSHANSY ET AL.) 23 September 1975 cited in the application see claims 1-6 ---	1-14 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*'A' document defining the general state of the art which is not considered to be of particular relevance
- \*'E' earlier document but published on or after the international filing date
- \*'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*'O' document referring to an oral disclosure, use, exhibition or other means
- \*'P' document published prior to the international filing date but later than the priority date claimed

- \*'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*'A' document member of the same patent family

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Date of the actual completion of the international search

23 April 1996

Date of mailing of the international search report

15.05.96

Name and mailing address of the ISA

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Authorized officer

Decocker, L

**INTERNATIONAL SEARCH REPORT**Int'l Application No  
PCT/US 95/16378

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

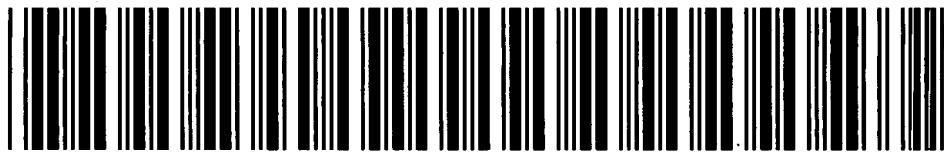
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 634 435 (GENERAL ELECTRIC COMPANY) 18 January 1995 see claims 1-9,13-25 -----	1-10

1

**INTERNATIONAL SEARCH REPORT**International Application No  
PCT/US 95/16378

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4250078	10-02-81	US-A-	4420581	13-12-83
US-A-3907754	23-09-75	NONE		
EP-A-634435	18-01-95	US-A-	5453479	26-09-95
		JP-A-	7138354	30-05-95

# IDS REFERENCES



FOR

29

⑨ 日本国特許庁 (JP)      ⑩ 特許出願公開  
 ⑪ 公開特許公報 (A)      昭59—46258

⑤Int. Cl.<sup>3</sup>  
 C 07 C 121/75  
 120/00

識別記号      廣内整理番号  
 7731—4H  
 7731—4H

⑩公開 昭和59年(1984)3月15日  
 発明の数 1  
 審査請求 有

(全 7 頁)

⑫4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造方法

⑬特 願 昭58—101594

⑭出 願 昭58(1983)6月7日

優先権主張 ⑬1982年6月7日 ⑮米国(US)  
 ⑯385609

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 ツチモンド・サウス・フォース  
 ・ストリート330

⑮代理人 弁理士 浅村皓 外2名

明細書の序説(内容に変更なし)

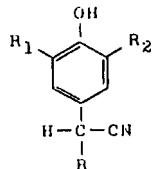
明細書

1. 発明の名称

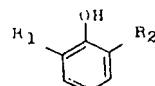
4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造方法

2. 特許請求の範囲

(1) 式



(式中、Rは水素、メチル、エチル、n-プロピルまたはイソプロピルであり、R<sub>1</sub>およびR<sub>2</sub>はアルキル、アラルキルおよび環式アルキル基からなる群から選ばれる同一または異なる1個の置換基である)を有する4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造方法において、式



(式中、R<sub>1</sub>およびR<sub>2</sub>は前記に定義された通りである)

を有するジ-置換フェノールをホルムアルデヒド、アセトアルデヒド、プロピオンアルデヒド、ブチルアルデヒドまたはイソブチルアルデヒドから選ばれる脂肪族アルデヒドおよびシアン化アルカリ金屬またはシアン化アルカリ土類金屬と、適当な反応溶媒中において反応させて、前記4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールを形成することを特徴とする、4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造方法。

(2) R<sub>1</sub>およびR<sub>2</sub>は1個ないし約40個の炭素原子を含有するアルキル、アラルキルおよび環式アルキル基からなる群から選ばれる同一または異なる1個の置換基であることをさらに特徴とする、特許請求の範囲第1項の方法。

(3) シアン化アルカリ金屬がシアン化ナトリウムであることをさらに特徴とする、特許請求の範囲第1項の方法。

(4) 溶媒が、双極性中性溶媒であることをさらに特徴とする、特許請求の範囲第1項の方法。

(5) 溶媒がジメチルスルホキシド、N,N-ジメチル-ホルムアミド、N,N-ジメチルアセトアミド、ジメチルスルホン、テトラメチレンスルホン、N-メチルピロリジノンおよびアセトニトリルからなる群から選ばれることをさらに特徴とする、特許請求の範囲第4項の方法。

(6) 溶媒が、1個ないし約6個の炭素原子を有する低級アルカノールからなる群から選ばれることをさらに特徴とする、特許請求の範囲第4項の方法。

(7) 反応が、高温において行われることをさらに特徴とする、特許請求の範囲第1項の方法。

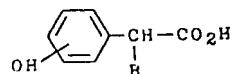
(8) 方法が少なくとも50°Cの温度において行われることをさらに特徴とする、特許請求の範囲第7項の方法。

### 3. 発明の詳細な説明

本発明は、4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの新規な製

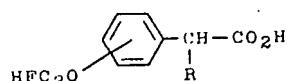
造方法に関する。さらに、本発明は、新規な合成反応において製造され、しかも $\alpha$ -アルキル-4-ヒドロキシフェニル酢酸が製造され次いで $\alpha$ -フエノキシベンジルおよび $\alpha$ -シアノ- $\alpha$ -フエノキシベンジルエステルの殺虫剤の製造における反応中間体として使用される反応系列において中間体として使用される4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールに関する。

2-ハロアルキル(オキシ-、チオ-、スルフィニル-、またはスルホニル)フェニルアルカン酸の $\alpha$ -フエノキシベンジルエステルおよび $\alpha$ -シアノ- $\alpha$ -フエノキシベンジルエステルは既知の殺虫剤および殺ダニ剤である。これらの化合物およびそれらの製造方法はBerkelhammerらの米国特許第4,178,460号および第4,199,595号明細書に開示されている。これらのBerkelhammerらの米国特許第4,178,460号および第4,199,595号の明細書において、式



(式中、Rはエチル、n-プロピルまたはイソブロピルである)

を有する若干の $\alpha$ -アルキル-3(または4)-ヒドロキシフェニル酢酸を、水性アルカリおよびジオキサン中においてクロロジフルオロメタンをもつて処理することによる相当する式



(式中、Rは前記に定義された通りである)を有する $\alpha$ -アルキル-(3または4)-ジフルオロメトキシフェニル-酢酸への変換が開示されている。このようにして形成された $\alpha$ -アルキル-3(または4)-ジフルオロメトキシフェニル酢酸は、次いで好ましくはベンゼンまたはトルエンのような芳香族溶媒の存在下に塩化チオニル、臭化チオニルなどをもつて処理されてハロゲン化 $\alpha$ -

アルキル(置換フェニル)アセチルを生成し、このハロゲン化 $\alpha$ -アルキル(置換フェニル)アセチルは $\alpha$ -フエノキシベンジルアルコールまたは $\alpha$ -シアノ- $\alpha$ -フエノキシベンジルアルコールと反応されて殺虫剤として有用な重要な2-ハロアルキル(オキシ-、チオ-、スルフィニル-またはスルホニル)フェニルアルカン酸の $\alpha$ -フエノキシベンジルエステルまたは $\alpha$ -シアノ- $\alpha$ -フエノキシベンジルエステルを生成する。

Berkelhammerらの米国特許第4,178,460号および第4,199,595号明細書において、 $\alpha$ -アルキル-3(または4)-ヒドロキシフェニル酢酸中間体は、適切な $\alpha$ -アルキル-3(または4)-メトキシフェニルアセトニトリルを臭化水素酸と反応させることによつて製造される。

$\alpha$ -アルキル-4-ヒドロキシフェニル酢酸が単純かつ直接的なやり方で製造できる、この物質の新しい合成方法が今や発見された。この新しい方法において、4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールは、新規

な合成反応において製造され、しかも $\alpha$ -アルキル-4-ヒドロキシフェニル酢酸が同様に製造されかつ反応中間体として用いられる反応系列において中間体として使用される。

4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造方法は既知である。例えば、ハロゲン化 $\alpha$ -アルキル-4-ヒドロキシ-3,5-ジ-tert-ブチルベンジルをシアノ化ナトリウムと反応させることによる4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造は、A. A. Volod'kin らの Iz. Akad. Nauk. SSSR. Ser. Khim. 1966, 1031によつて報告されている。また、相当する2,6-ジ-置換メチレン-キノンの電気化学的還元による4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの製造は、L. I. Kudinova らの Iz. Akad. Nauk. SSSR. Ser. Khim. 1978, 1313によつて報告されている。

また、o-およびp-ヒドロキシ置換フェニル

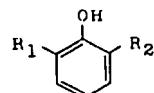
(式中、各Rはアルキル、アラルキルおよび環式アルキル基から選ばれる同一または異なる1価の置換基を有するフェノールである。これらのフェノールは、ホルムアルデヒド、アセトアルデヒド、プロピオンアルデヒド、ブチルアルデヒドまたはイソブチルアルデヒドおよびシアノ化アルカリ金属またはシアノ化アルカリ土類金属と液相において反応される。

置換基R<sub>1</sub>およびR<sub>2</sub>が、望ましい4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの形成または4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールの以後の脱アルキルの何れかを妨げずに相当する4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)フェノールを生成する限り、R<sub>1</sub>およびR<sub>2</sub>の可能なアルキル、アラルキルおよび置換アルキル基の代表例としては、任意数の炭素原子を有する前記の基の何れかがある。これらの基は、1個ないし4個またはそれ以上の炭素原子を含んでもよく、しかもアルキル基としては、第一、第二または第三ア

セトニトリルの合成も既知であり、しかも文献に報告されている。例えば、ジャーナル・オブ・オーガニック・ケミストリー (Journal of Organic Chemistry)、Vol. 41、No. 14、2502 (1976) に報告されている。

従つて、本発明には、2,6-ジ-置換フェノールをホルムアルデヒド、アセトアルデヒド、プロピオンアルデヒドまたはブチルアルデヒドから選ばれる脂肪族アルデヒドおよびシアノ化アルカリ金属またはシアノ化アルカリ土類金属と、適當な反応溶媒中において反応させて相当する4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールを形成することによって、4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールを好収率かつ高選択性で容易に製造できるという発見が含まれる。

本発明の方法において、出発物質として使用できるフェノールは、一般式



ルキル基およびシクロアルキル基がある。置換フェノールの最も容易に入手できるものは1個ないし約8個の炭素原子の置換基を有するフェノールであるため、これらは好ましいが、本発明はこれらに限定されない。代表的な置換基の例としては、メチル、エチル、プロピル、イソプロピル、異性体ブチル基(すなわちリ-ブチル、イソブチル、シクロブチル、tert-ブチルなど)、異性体アミル基、異性体ヘキシル基、異性体デシル基、異性体ヘキサデシル基、異性体エイコシル基、異性体トリコシル基、異性体トリアコンチル基などがある。アルキル基はアリール、好ましくはモノ環式アリール基、またはシクロアルキル基、例えばベンジル、フェニルエチル、シクロヘキシルエチル、ナフチルエチルなどをもつて置換されてもよい。アリール基の例は、フェニル、トリル、キシリル、ビフェニリル、ナフチル、メチルナフチル、エチルフェニル、シクロヘキソフェニルなどである。R置換基がメチル、エチル、プロピル、ブチル、sec-ブチル、イソプロピル、tert-ブチル、ア

ミル、sec-アミル、tert-アミル、ヘキシル、ヘナチル、オクチルなどあるいはフェニルであるフェノールが商業的に容易に入手できるかまたは容易に製造でき、しかも方法に理想的に適しているため、最も好ましい置換基は、R<sub>1</sub>およびR<sub>2</sub>が低級アルキル基（すなわち1個ないし約8個の炭素原子）またはフェニルである。

前記のR置換基を有する、好ましい出発物質のフェノールの例としては、2,6-ジ-メチルフェノール、2,6-ジ-sec-ブチルフェノール、2,6-ジ-イソプロピルフェノール、2,6-ジ-sec-オクチルフェノール、2,6-ジ-(α-メチルベンジル)フェノール、2-アミル-6-メチルフェノール、2,6-ジベンジルフェノール、2-メチル-6-ベンジルフェノールなどがある。この方法の実施における使用に特に好ましいフェノール反応体は2,6-ジ-tert-ブチルフェノールである。

前記以外のアリール、塩基、堿素、フッ素、二トロ基などのような置換基Rは、これらの置換基

用いて与えられる液相中において行われる。すなわち、反応は、反応に加わらない溶媒の存在下に行われる。好ましい溶媒は、ジエチルエーテル、ジブチルエーテル、1-エトキシヘキサン、テトラヒドロフラン、1,4-ジオキサン、1,3-ジオキソラン、ジグライム、1,2-ジエトキシエタンのようなエーテルおよびピリジン、N-エチルピペリジン、トリエチルアミン、トリブチルアミン、N,N-ジフェニル-N-メチルアミン、N,N-ジメチルアラニンなどの第三アミンを含む非プロトン系溶媒である。特に好ましい溶媒はジメチルスルホキシド、N,N-ジメチル-ホルムアミド、N,N-ジメチル-アセトアミド、ジメチルスルホン、テトラメチレンスルホン、N-メチルピロリジノン、アセトニトリルおよび同様の物質のような双極性中性溶媒である。反応条件下で不活性の他の溶媒、例えば低沸点炭化水素、ハロゲン化炭化水素を使用してもよい。これらの例は、ベンゼン、トルエン、テトラクロロエタン、塩素化ベンゼン、塩素化トルエンなどである。さらに、約6

が4-(α-アルキル-α-シアノ-メチル)-2,6-ジ-置換フェノールの形成あるいは縮合反応生成物の相当する4-(α-アルキル-α-シアノ-メチル)フェノールの以後の脱アルキルに影響を与えない条件で、芳香族フェノール化合物の2位および6位に存在してもよい。

この方法に用いられるアルデヒド反応体は、單一アルデヒドを有するアルデヒドであり、しかもホルムアルデヒド、アセトアルデヒド、プロピオンアルデヒド、ブチルアルデヒドまたはイソ-ブチルアルデヒドから選ばれる。

本方法に用いられるシアノ化アルカリ金属およびシアノ化アルカリ土類金属反応体としてはシアノ化ナトリウム、シアノ化カリウム、シアノ化リチウム、シアノ化マグネシウムおよびシアノ化カルシウムがある。また、シアノ化アンモニウムおよびシアノ化水素は本方法の実施において使用できる。シアノ化ナトリウムは好ましいシアノ化物反応体である。

この反応は、反応条件下で不活性である溶媒を

個までの炭素原子を有する低級アルカノールも使用できる。これらの低級アルカノールとしては、メタノール、エタノール、n-ブロパノール、イソプロピルアルコール、n-ブタノール、sec-ブチルアルコール、tert-ブチルアルコール、n-ペンタノール、イソペンチルアルコール、n-ヘキサン、イソヘキシルアルコールがある。さらに、反応混合物中のシアノ化物含有反応体の可溶化を容易にするためこの反応混合物に少量の水を加えてもよい。

反応は、攪拌手段を有する反応器に2,6-ジ-置換フェノールおよび他の反応混合物成分を入れることによって容易に行われる。この方法は、実質的に無水の反応系において行われるのが好ましく、従つて反応系の成分は、実質的に乾燥した不活性のふん甾気の下に一概にされかつ保持されなければならない。従つて、水を反応混合物に加える場合のように空気または水分の存在下にこの方法を行うことができるが、反応系を乾燥した塩素などのふん甾気の下に保つのが望ましい。

添加の方式は特に重要ではない。従つて、フェノール反応体を他の材料の混合物に加え、アルデヒド反応体を他の材料の混合物に加え、シアノ化物反応体を他の材料の混合物に加え、全成分を同時に反応常域などに導入するのが適当である。この方法は、実験的にすべてのフェノール反応体を相当する4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノール中間体に変換するに十分な時間行わなければならない。一般に、最高収率のための時間の長さは、主に反応温度および反応に使用される特別の溶媒によつて決まる。しかしながら、反応は通常、非常に迅速に進み、従つて長い反応時間は必要ない。反応は、反応条件においてはば分または多くて数時間で完了できる。

反応は、環境温度において非常に迅速で進むが、反応を少なくとも約50°Cないし反応体または生成物の何れかの分解温度までの高温で行うのが適当である。環境大気圧または環境圧力より低圧または高圧を使用できる。しかしながら、環境圧力

シアノ化物反応体の両者の過剰を用いるのが望ましい。通常、反応系はフェノール反応体1モルについてアルデヒド少なくとも1モル当量およびシアノ化物少なくとも1モル当量を含有し、しかもアルデヒド対シアノ化物のモル比は2またはそれ以上が好ましい。

本発明の実施は、下記の例示的例によつてさらに明らかになる。

#### 例1

##### ( $\alpha$ -シアノ-メチル)-2,6-ジ-tert-ブチルフェノールの製造

2,6-ジ-tert-ブチルフェノール(2.06g、10ミリモル)、シアノ化ナトリウム(1.47g、3.0ミリモル)、パラホルムアルデヒド(0.72g、2.4ミリモル)およびジメチルホルムアミド(8ml)を180mlのフイツシャー-ボーター管(Fisher-Porter tube)に装入し、留置をもつて125psigに加圧し、次いで9時間140°C(油浴温度)に加熱した。得られた反応混合物を環境温度に放冷し、次いでこの混合物を水に加え、

よりも低圧を用いるのは有利でない。若しも反応混合物の環境条件における沸点よりも高圧を用いるならば、通常、環境圧力より高圧条件が用いられる。しかしながら、離まれる液相を形成するために溶媒を適切に選択することによつて、温度は、約50°Cないし適当な反応速度を与える環境大気条件における反応混合物の過渡温度までの範囲内に達し得る。

本発明の実施に従い、2,6-ジ-置換フェノールの相当する4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-2,6-ジ-置換フェノールへの変換により、未反応フェノール、4-( $\alpha$ -アルキル- $\alpha$ -メチル)-2,6-ジ-置換フェノールおよびビス-(3,5-ジ-tert-ブチル-4-ヒドロキシフェニル)アルキルメタンのような副生物が実質的に非常にわずかに形成される。生成物の回収は、蒸発および水洗または適当な有機溶媒による抽出のような従来の手段によつて行われる。

最高の結果については、2,6-ジ-置換フェノール反応体に関してアルデヒド反応体およびシア

ノ化物反応体の両者の過剰を用いるのが望ましい。通常、反応系はフェノール反応体1モルについてアルデヒド少なくとも1モル当量およびシアノ化物少なくとも1モル当量を含有し、しかもアルデヒド対シアノ化物のモル比は2またはそれ以上が好ましい。

#### 例2

##### 4-( $\alpha$ -イソプロピル- $\alpha$ -シアノ-メチル)

##### -2,6-ジ-tert-ブチルフェノールの製造

2,6-ジ-tert-ブチルフェノール(21.42g、103.8ミリモル)、シアノ化ナトリウム(15.29g、31.2ミリモル)、イソブチルアルデヒド(17.99g、25.0ミリモル)およびジメチルホルムアミド(83ml)を180mlのフイツシャー-ボーター管に装入し、次いで留置をもつて125psigに加圧し、次いで9時間140°C(油浴温度)に加熱した。得られた反応混合物を環境温度に放冷し、次いで混合物を水150mlに注入し、ジエチルエーテルをもつて抽出した。このエーテル層を乾燥(MgSO<sub>4</sub>)、ろ過

して、エーテルをロータリーエバボレーター中で除いた。残留物をエタノール約30 mlに溶解し、次いで氷を徐々に加えて沈殿させて4-( $\alpha$ -イソプロピル- $\alpha$ -シアノ-メチル)-2,6-ジ-tert-ブチルフェノールの収量27.05 g (90.7%)を生じた。

前記例2と同様の方法で、温度、反応時間、圧力および反応体の比率を変更して多数の実験を行つた。結果は、内部標準をもつて気相クロマトグラフィーによつて分析され、第1表に示される。

第1表

4-( $\alpha$ -イソプロピル- $\alpha$ -シアノ-メチル)-2,6-ジ-tert-ブチルフェノールの製造

実験 no.	2,6-ジ-tert- ブチルフェノール (ミリモル)	イソブチル- アルデヒド (ミリモル)	NaCN (ミリモル)	溶媒 (ml.)	温度 (°C)	圧力 (psi)	時間 (hr.)	% 収率
3	10	24	30	DMP-8 ml.	95	125	7	58.5
4	10	24	30	iOH-8 ml.	140	125	7	47.0
5	10	24	30	DMP-8 ml.	135	125	7	78
6	80	192	240	DMP-64 ml.	140	125	9	86
7	10	24	30	toluene-8 ml.	135	125	5	trace
8	103.8	207.6	207.6	DMP-83 ml.	140	125	9	94.5
9	103.8	250	114.1	DMP-83 ml.	140	125	9	54.0
10	103.8	200	119.4	DMP-83 ml.	140	125	9	84.0
11	10	24	30	イソブチルアルコール -8 ml.	95	125	7	14.2
12	10	12	30	iOH-8 ml.	95	125	2.5	66.4
13	103	250	207	DMP-83 ml.	140	100	9	92
14	103	250	207	DMP-83 ml/5% H <sub>2</sub> O	140	100	4	75
15	100	200	125	DMP-83 ml/5% H <sub>2</sub> O	140	100	9	71
16	103.8	250	207	DMP-83 ml/5% H <sub>2</sub> O	140	80	9	83.1
17	103.8	250	207.6	MeOH-83 ml.	140	105	5.5	91.7
18	103.8	175	155.7	MeOH-83 ml.	140	100	3	87
19	100	175	150	MeOH-85 ml.	140	80	3	95
20	100	150	125	MeOH-85 ml.	140	80	3	82.4

## 手 続 補 正 書 (自発)

昭和 58 年 7 月 27 日

特許庁長官殿

## 1. 事件の表示

昭和 58 年特許第 101594 号

2. 発明の名称 4-( $\alpha$ -アルキル- $\alpha$ -シアノ-メチル)-  
-2,6-ジ-置換フェノールの製造方法

## 3. 補正をする者

事件との関係 特許出願人

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## 5. 補正命令の日付

昭和 年 月 日

## 6. 補正により増加する発明の数

## 7. 補正の対象 明細書

8. 補正の内容 別紙のとおり  
明細書の削除 (内容に変更なし)